

4.5.4 Radiochemical

Americium

Am-01-RC

AMERICIUM IN SOIL

Contact Person(s) : Anne Berne

APPLICATION

This procedure is applicable to soils which contain americium deposited from worldwide fallout and some nuclear activities.

Americium is leached from the soil with HNO_3 and HCl and simultaneously equilibrated with ^{243}Am tracer. The soil is processed through the plutonium separation steps using ion exchange resin according to Procedure Pu-11-RC. If determination of plutonium is desired, an appropriate plutonium tracer should be added along with the ^{243}Am tracer. Americium is collected with a calcium oxalate precipitation and finally isolated and purified by ion exchange. After source preparation by microprecipitation, the ^{241}Am is determined by alpha spectrometry using ^{243}Am tracer to provide recovery data.

SPECIAL APPARATUS

1. For microprecipitation, see Procedure G-03.
2. Ion-exchange columns - see Specification 7.5.

SPECIAL REAGENTS

1. Americium-243 tracer solution, about 0.15 Bq g^{-1} in dispensing bottle - standardize for total disintegration rate. Measure purity on an α spectrometer.

2. Bio-Rad AG 1-X8 resin (100-200 mesh) - see Specification 7.4.
3. Bio-Rad AG 1-X4 resin (100-200 mesh) - see Specification 7.4.
4. 4M ammonium thiocyanate solution - dissolve 304 g of NH_4SCN in deionized distilled water and dilute to 1 L. To purify the 4M NH_4SCN , place 4 L of solution in a 5 L polyethylene beaker. Add 25 mL of Bio-Rad AG 1-X4 resin (100-200 mesh) ion exchange resin, and mix for 1 h with a magnetic stirrer. Allow the resin to settle and filter by gravity through Whatman No. 40 filter paper. Repeat the addition of the resin and filtration steps twice more to remove all Fe^{+3} from the 4M NH_4SCN . Store the purified 4M NH_4SCN in a polyethylene bottle.
5. 0.4M NH_4SCN - 0.3M HCl - dilute 100 mL of purified 4M NH_4SCN to 500 mL with water, then add 25 mL HCl and dilute to 1 L. Make 2 L of solution for 10 samples.
6. Calcium carrier solution, 100 mg mL^{-1} - dissolve 25 g CaCO_3 in a minimum of HNO_3 and dilute to 100 mL.
7. Iron carrier, 100 mg mL^{-1} - slowly heat 100 g of iron powder in 500 mL of HCl until reaction ceases. Carefully and slowly add 100 mL of HNO_3 while stirring. Cool and dilute to 1 L.
8. Oxalate wash solution - dissolve 10 g of oxalic acid to make 1 L of solution (~ 1% solution).

SAMPLE PREPARATION

1. Weigh 1000 g of soil into a 4-L beaker. Add a weighed amount (about 0.03 Bq) of ^{243}Am tracer.
2. Slowly add 900 mL of HNO_3 . Control the foam with the addition of a few drops of n-octyl alcohol. When the reaction subsides, add 300 mL of HCl . Allow the mixture to react at room temperature, then heat on a low temperature hot plate overnight with occasional stirring.

3. Dilute to 1:1 HNO_3 and filter through Whatman No. 42 filter paper into a 3-L flask. Wash with 1:1 HNO_3 . Retain the filtrate. Return the residue and filter to the original beaker.
4. Add 900 mL of HNO_3 and wet ash the filter paper. Maintain the HNO_3 volume. Cool and add 300 mL of HCl to the residue and heat on a low temperature hot plate for about 3 h with occasional stirring. Cool and allow to settle overnight.
5. Filter and wash as in Step 3. Combine the filtrate with the filtrate from Step 3. Return the residue and filter to the original beaker.
6. Repeat Step 4.
7. Filter and wash as in Step 3. Combine the three filtrates and discard the residue.
8. Decompose any organic matter in the extract by heating with repeated additions of HNO_3 , covering the sample with a watch cover and letting the sample reflux. Concentrate until salting out begins to occur. Add an equal volume of water. If solution is not clear, proceed to Step 9, otherwise go to Step 14.
9. If any siliceous matter is present, filter by gravity over an 18.5 cm Whatman No. 42 filter paper. Wash the residue with 1:1 HNO_3 . Reserve the filtrate.
10. Transfer the filter paper with the residue to the original beaker and ash the paper with 100 mL of HNO_3 . Repeat two or three times, then transfer the residue into a 100-mL platinum dish using 1:1 HNO_3 .
11. Add 5-25 mL of HF and 5-25 mL of HNO_3 to the platinum dish and evaporate on a medium temperature hot plate. Repeat the addition of the HF/HNO_3 and the evaporation process two or three times. Rinse the walls of the platinum dish with 1:1 HNO_3 and evaporate. Repeat three times. Evaporate to dryness. Dissolve with 1:1 HNO_3 and evaporate to dryness.
12. Dissolve the residue in 1:1 HNO_3 and filter by gravity through a Whatman No. 42 filter paper. Add the filtrate to the solution from Step 9. Discard the filter and any residue.

13. Heat the combined solution (with the addition of HNO_3 if necessary) to complete the oxidation of any organic materials. Evaporate to near dryness. Redissolve in 1:1 HNO_3 and stir to get a clear solution, adding 1:1 HNO_3 as necessary.
14. Proceed to Procedure Pu-11-RC, ion-exchange purification saving the column effluents for **Americium Determination**.

AMERICIUM DETERMINATION

1. Evaporate the americium effluents to incipient dryness. Redissolve in a minimum amount of 1:1 HNO_3 , dilute with four volumes of water.
2. Add 5 mL of calcium carrier solution (500 mg of calcium) and 50 g L^{-1} of oxalic acid to the sample while stirring with a magnetic stirrer. (The total volume of the sample solution can be estimated using the markings on the beaker, and the amount of oxalic acid to be added is calculated using that volume.)
3. Adjust the pH of the solution to 2.0 - 2.5 with NH_4OH using pH paper as an indicator and continue to stir for 30 min. Remove the magnetic stir bar.
4. Cool and let stand until precipitate settles and solution clears (for more than 6 h or overnight). Check for completeness of precipitation using a drop of saturated $\text{H}_2\text{C}_2\text{O}_4$ solution. Aspirate (or decant), using a disposable transfer pipette and suction, as much liquid as possible without disturbing the precipitate. Transfer the precipitate to a 250-mL centrifuge bottle using oxalate wash solution (see **Note 1**). Balance the bottles on a double pan balance and centrifuge for 10 min at 2000 rpm. Decant and discard the supernate.
5. Break up the precipitate with a stirring rod and wash the precipitate with the oxalate wash solution. Centrifuge, decant and discard the wash. Repeat wash. Redissolve the precipitate in a minimal amount (50-70 mL) of concentrated HCl (redissolve the precipitate in ~200 mL of HNO_3 a final time and proceed to Step 8). (**Note:** Dissolution is easier if the centrifuge bottle is placed in a hot water bath and stirred with a glass rod).

6. Transfer the dissolved precipitate to the original 600-mL beaker. Add enough water to make ~ 1M solution. Add 50 g L⁻¹ of oxalic acid.
7. Repeat Steps 3 through 6 until supernate is colorless.
8. Transfer the dissolved precipitate to the original beaker and heat to destroy the oxalate ion. Evaporate to near dryness. Dissolve in minimum 1:1 HNO₃. Transfer to centrifuge bottle using water to complete the transfer.
9. Add enough water to make ~1M HNO₃. Warm the solution in a 90° hot water bath and add 0.2 mL iron carrier solution (20 mg iron).
10. With the centrifuge bottle in the hot water bath adjacent to a hood, adjust the pH of the solution to 8-9 with NH₄OH while stirring with a glass rod. Allow solution to digest in a hot water bath for 20 min.
11. Cool in a cold water bath, rinse, and remove the glass rod. Balance the bottles on a double pan balance and centrifuge for 40 min at 2000 rpm.
12. Decant (or aspirate) and discard the supernate. Add 10 mL concentrated HCl to dissolve the Fe(OH)₃ pellet. Add four drops 30% H₂O₂ to oxidize any Mn present, followed by 100 mL of water. Heat in the water bath for 30 min to get rid of the excess H₂O₂.
13. Repeat Steps 10 to 12 three times. Reprecipitate, centrifuge and redissolve. The final precipitate should be redissolved in HNO₃.
14. Transfer to a 250-mL beaker, evaporate to dryness, add 20 mL HNO₃, and evaporate to dryness again.
15. Dissolve the wet-ashed residue in 40 mL 1:1 HNO₃. Cool in an ice-water bath. Add 0.6-1.0 g NH₂OH · HCl, dissolve, and let the solution react for 15 min. Cover with a watch glass. Heat on a low temperature hot plate to decompose unreacted NH₂OH · HCl, then bring to a gentle boil for 1-2 min. Cool and pass the solution through a 1:1 HNO₃ ion-exchange column (see **Note 2**). Collect the effluent in a 400-mL beaker. Wash the column with 150 mL of 1:1 HNO₃, and collect in the beaker.

16. Evaporate the sample in the 400-mL beaker to dryness. Convert to HCl by adding 20-30 mL of HCl at a time, heat to almost dryness, and repeat the HCl addition and evaporation at least three times. Evaporate again and dissolve the final residue in 30 mL of HCl. Pass this solution through a 12N HCl ion exchange column (see **Note 3**). Collect the effluent in a 250-mL beaker. Wash with 100 mL of HCl, and collect in the 250-mL beaker.
17. Evaporate to dryness. Dissolve in 1-2 mL of HCl. Cool thoroughly. Add 40 mL of 4M NH₄SCN and stir immediately. Stir the sample and pass the solution through a 4M NH₄SCN column (see **Note 4**). Discard the effluent.
18. Wash the column with 200 mL of 4N NH₄SCN solution. Discard the wash solution.
19. Elute the americium into a 250-mL beaker with 180 mL of 0.4N NH₄SCN - 0.3N HCl. Evaporate to dryness on a low temperature hot plate overnight. Discard the resin.
19. To remove NH₄⁺ salts, place the beaker on an iron tripod and heat slowly with a cool Bunsen flame. After ~ 0.5 h, increase the flame temperature and continue heating to remove all NH₄⁺ salts and S, then heat briefly to dull red heat. This step requires ~ 1-1.5 h.
20. Cool to room temperature. Add 25 mL of HNO₃ and boil slowly for a few minutes. **Cautiously** add 1 mL of 30% H₂O₂ and evaporate the solution to dryness.
21. Convert the residue to Cl⁻ by adding 1 mL of HCl and evaporating to dryness twice and proceed to microprecipitation.

Notes:

1. If a centrifuge is not available, centrifugation can be replaced by filtering and wet ashing the filter paper and precipitate in HNO₃
2. Preparation of 1:1 HNO₃ Column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer with deionized distilled water, 15 mL of wet settled Bio-

Rad AG 1-X8 resin (100-200 mesh) to the column and allow it to settle. Place a second plug of glass wool on top of the resin and with the stopcock open allow the H₂O level to reach the top of the upper plug. Pass 150 mL of 1:1 HNO₃ through the resin bed in three 50-mL portions or enough so that the effluent tests free of Cl⁻ ion using dilute silver nitrate solution, allowing the level of each portion to reach the top of the upper glass wool plug.

3. Preparation of HCl Column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer 10 mL of wet settled Bio-Rad AG 1-X4 resin (100-200 mesh) with deionized water to the column and allow it to settle. Place a second plug of glass wool on top of the resin and with the stopcock open allow the H₂O level to reach the top of the upper plug. Pass two 50-mL volumes of HCl through the resin bed and allow each to reach the top of the upper glass wool plug.
4. Preparation of NH₄SCN Column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer with deionized distilled water, 15 mL of wet settled Bio-Rad AG 1-X4 resin (100-200 mesh) to the column and allow it to settle. Place a second plug of glass wool on top of the resin and with the stopcock open allow the H₂O level to reach the top of the upper plug. Pass 100 mL of purified 4M NH₄SCN through the resin bed in two 50-mL portions, allowing the level of each portion to reach the top of the upper glass wool plug.

MICROPRECIPITATION

See Microprecipitation Source Preparation for Alpha Spectrometry, Procedure G-03.

DATA PROCESSING AND ANALYSES

For alpha spectrometry measurements, please see Procedure A-01-R.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	25
Counter Background	(cps)	15×10^{-6}
Yield	(%)	50
Blank	(cps)	-
LLD (400 min)	(mBq)	1
LLD (1000 min)	(mBq)	0.5
LLD (5000 min)	(mBq)	0.3

Am-02-RC

AMERICIUM-241 IN SOIL - GAMMA SPECTROMETRY

Contact Person(s) : Colin G. Sanderson

APPLICATION

This procedure is capable of determining small amounts of ^{241}Am in large volume soil samples. The lower limit of detection for 600-800 g of soil in a Marinelli beaker is 0.74 mBq for a 1000-min count.

Americium-241 decays with the emission of γ rays at 11.9, 13.9, 17.8, 20.8, 26.4, and 59.5 keV. The 59.5 keV γ ray, which has an abundance of 35.9%, can be measured in soil with commercially available germanium (Ge) semiconductor γ -ray detectors and 600 mL Marinelli beakers. Gamma-ray attenuation corrections are required if the calibration source and the sample are in a different matrix or are of different densities.

SPECIAL APPARATUS

1. Hyperpure Ge γ -ray detector, shield, and associated electronics.
2. Multichannel analyzer.
3. Marinelli beaker - see Specification 7.22.

SPECIAL REAGENT

Americium-241 calibration solution, about 2.50 Bq mL^{-1} .

SPECTROMETER CALIBRATION

1. Transfer 600 mL of standardized ^{241}Am solution to a Marinelli beaker.
2. Set the spectrometer energy calibrations at 0.5 keV/channel and count the standard until 10,000 or more counts are accumulated in the channels corresponding to 58.0 to 61.5 keV.
3. Record the count time and the channel-by-channel data corresponding to 56.0 to 63.5 keV.

SAMPLE PREPARATION

1. Transfer 600 mL of prepared soil to a Marinelli beaker.
2. Accumulate sufficient counts in the 59.5 keV ^{241}Am peak to achieve the desired counting statistics.
3. Record the count time and the channel-by-channel data corresponding to 56.0 to 63.5 keV.

DETERMINATION

If computer calculation techniques are used to determine peak areas from spectral data, the same techniques must be used for both calibration standards and samples. However, in most instances, simple peak integration by channel summing is sufficient.

The net count in the ^{241}Am peak = $A - B - C$.

where

A = sum of counts in the 8 channels from 58.0 to 61.5 keV

B = sum of counts in the 4 channels from 56.0 to 57.5 keV

C = sum of counts in the 4 channels from 62.0 to 63.5 keV

B and C are the leading and trailing edges of the photopeak and represent the background upon which the photopeak is superimposed.

The net ^{241}Am counts, AmC, corrected for attenuation equals

$$A/e^{-(\mu d \cdot w)}$$

where

A = observed net counts in the ^{241}Am peak,

μd = attenuation constant for Marinelli beaker (see Note below),
for H_2O , $\mu d = 0.000427 \text{ cm}^2 \text{ g}^{-1}$
for soil, $\mu d = 0.000533 \text{ cm}^2 \text{ g}^{-1}$

w = weight in g of the standard or sample.

The ^{241}Am detector efficiency at 59.5 keV,

$$\text{Efficiency} = (\text{AmC}/t)/(\text{Ac} \cdot 600)$$

where

AmC = net ^{241}Am counts of the standard, corrected for attenuation, and

t = standard count time (sec).

Ac = ^{241}Am activity of standard (Bq mL^{-1}).

The $\text{Bq } ^{241}\text{Am}$ in the sample = $(\text{AmC}/t)/\text{Efficiency}$

where

$AmC =$ net ^{241}Am counts of the sample, corrected for attenuation, and

$t =$ sample count time (sec).

Note:

The Marinelli beaker attenuation constant ($\mu_d = 0.000533 \text{ cm}^2 \text{ g}^{-1}$) is for soil of normal composition. Soils or ores composed of high atomic number elements will require a different constant. For example, a 1% U ore will attenuate the 59.5 keV γ ray to 7% more than normal soil and the correct μ_d would be $0.000677 \text{ cm}^2 \text{ g}^{-1}$.

Am-03-RC

AMERICIUM IN WATER, AIR FILTERS, AND TISSUE
(see Volume II)

Am-04-RC

AMERICIUM IN QAP WATER AND AIR FILTERS - EICHROM'S TRU RESIN

Contact Person(s) : Anna Berne

APPLICATION

The following procedure has been applied to the preparation, separation, and analysis of spiked water and air filter samples that contain americium but not lanthanides (Berne, 1996). Lanthanides, if present, will not be removed by this method and will significantly reduce the resolution of the α -spectrograph. Combined with Procedure Pu-11-RC, this procedure allows for the sequential determination of plutonium and americium. Other researchers have applied TRU Resin methods to other matrices (Horowitz et al., 1990). The procedure is used in the EML Quality Assessment Program (QAP; Sanderson and Greenlaw, 1996).

The water and air filters are equilibrated with ^{243}Am and processed through the plutonium separation steps using ion exchange resin according to Procedure Pu-11-RC. If determination of plutonium is desired, an appropriate plutonium tracer should be added along with the ^{243}Am tracer. The eluate from the ion exchange column containing americium (and all other ions, except plutonium) is evaporated, redissolved, and loaded onto a TRU Resin extraction column. The americium (and curium, if present) is separated and purified on the column and finally stripped with dilute nitric acid stripping solution. Microprecipitation is used to prepare for α spectrometry.

SPECIAL REAGENTS

1. Americium-243 tracer solution, about 0.15 Bq g^{-1} in dispensing bottle - standardize for total disintegration rate. Measure purity on an α spectrometer.

2. TRU Resin 2 mL ion extraction columns or equivalent or can be prepared from TRU Resin, Eichrom Industries, Inc., 8205 Cass AV, Suite 107, Darien, IL 60561. Place a plug of glass wool in the bottom of a polyethylene transfer pipette (see Specification 7.7). Add slurried TRU Resin (0.5 g). Assemble immediately before use.
3. Column feed solution, 0.5M $\text{Al}(\text{NO}_3)_3$ in 2M HNO_3 - place 18.76 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in a 100-mL volumetric flask and add 2M HNO_3 to the mark. Shake to mix thoroughly.
4. 2M HNO_3 - 125 mL HNO_3 diluted to 1 L with water.
5. 1M HNO_3 - 62.5 mL HNO_3 diluted to 1 L with water.
6. 0.025M HNO_3 - 25 mL 1M HNO_3 diluted to 1 L with water.

SAMPLE PREPARATION

See Procedure Pu-01-RC, air filters or Procedure Pu-10-RC, water.

AMERICIUM DETERMINATION

1. Collect the sample and the wash effluent from Step 4, **Ion Exchange Separation**, Procedure Pu-11-RC, and evaporate almost to dryness. If necessary, sometime during the evaporation process transfer the solution to a smaller beaker. The final residue should be contained in a beaker not larger than 50 mL. Add 3 mL of 0.5M $\text{Al}(\text{NO}_3)_3$ in 2M HNO_3 to each residue and heat very gently to dissolve.
2. Prepare an ion extraction column.
3. Wash the resin with 15 mL of 2M HNO_3 , and discard the effluent.
4. Load the column with the sample solution from Step 1. Wash the beaker with 3 mL of column-feed solution and add to the column. Discard the effluent.

5. Rinse the column with 8 mL of 2M HNO₃, followed by 8 mL of 1M HNO₃, and discard the effluents.
6. Elute the americium fraction with three 3-mL aliquots of 0.025M HNO₃, and collect the eluate in a 50-mL beaker.
7. Evaporate the eluate to dryness. Convert the residue to the chloride form by adding 5 mL of HCl three times and evaporating to dryness at a low temperature.
8. Prepare the sample for α spectrometry by microprecipitation (see Procedure G-03).

DATA PROCESSING AND ANALYSIS

For α spectrometry, see Alpha Radioassay, Procedure A-01-R.

LOWER LIMIT OF DETECTION (LLD)*

Counter Efficiency	(%)	30
Counter Background	(cps)	1.6×10^{-5}
Recovery	(%)	80
Blank	(cps)	-
LLD (400 min)	(mBq)	0.5
LLD (1000 min)	(mBq)	0.3
LLD (5000 min)	(mBq)	0.1

*Reagent blanks must be analyzed with each set of samples.

REFERENCES

Berne, A.

“Use of EICrom’s TRU Resin in the Determination of Americium, Plutonium and Uranium in Air Filter and water samples.”

USDOE Report EML-575, December (1995)

Sanderson, C. G. and P. Greenlaw

“Semi-Annual Report of the Department of Energy, Office of Environmental Restoration and Waste Management, Quality Assessment Program”

USDOE Report EML-581, July (1996)

Am-05-RC

AMERICIUM IN WATER AND AIR FILTERS
(see Volume II)

Am-06-RC

AMERICIUM AND/OR PLUTONIUM IN VEGETATION

Contact Person(s) : Anna Berne

APPLICATION

This procedure is applicable to vegetation which contain americium deposited from worldwide fallout and some nuclear activities. It is most effective when used on dried finely powdered samples of vegetation.

The vegetation is either dry ashed in a ceramic crucible using a muffle furnace or wet ashed with nitric acid. Wet ashing requires considerably more time and must be carefully attended to due to the highly reactive nature of vegetation. The sample is further digested with hydrofluoric acid to dissolve silicate compounds. Plutonium is separated by ion exchange and determined by alpha spectrometry. Americium is collected with a calcium oxalate precipitation and finally isolated and purified by ion exchange. After source preparation by microprecipitation, the ^{241}Am is determined by alpha spectrometry using ^{243}Am tracer to provide recovery data.

SPECIAL APPARATUS

1. For microprecipitation, see Procedure G-03.
2. Ion-exchange columns - see Specification 7.5.

SPECIAL REAGENTS

1. Americium-243 tracer solution, about 0.15 Bq g^{-1} in a dispensing bottle-standardize for total for total disintegration rate (and/or ^{236}Pu tracer solution - a standard solution containing $\sim 0.15 \text{ Bq g}^{-1}$ in a dispensing bottle). Measure purity on an α spectrometer.
2. Anion exchange resin, Bio-Rad AG 1-X8 resin (100-200 mesh) - see Specification 7.4.
3. Anion exchange resin, Bio-Rad AG 1-X4 resin (100-200 mesh) - see Specification 7.4.
4. TRU Resin 2 mL ion extraction columns or equivalent or can be prepared from TRU Resin, Eichrom Industries, Inc., 8205 Cass AV, Suite 107, Darien, IL 60561. Place a plug of glass wool in the bottom of a polyethylene transfer pipette (see Specification 7.7). Add slurried TRU Resin (0.5 g). Assemble immediately before use.
5. 0.5M $\text{Al}(\text{NO}_3)_3$ in 2M HNO_3 - place 18.76 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in a 100-mL volumetric flask and add 2M HNO_3 to the mark. Shake to mix thoroughly.
6. 2M HNO_3 - 125 mL nitric acid diluted to 1 L with water.
7. 1M HNO_3 - 62.5 mL nitric acid diluted to 1 L with water.
8. 0.025M HNO_3 - 25 mL 1M HNO_3 diluted to 1 L with water.
9. Calcium carrier solution, 100 mg mL^{-1} - dissolve 25 g CaCO_3 in a minimal amount of concentrated HNO_3 , dilute to 100 mL.
10. Iron carrier, 100 mg mL^{-1} - slowly heat 100 g of iron powder in 500 mL of HCl until the reaction ceases. Carefully and slowly add 100 mL of HNO_3 while stirring. Cool and dilute to 1 L.
11. Oxalate wash solution - dissolve 10 g of oxalic acid to make 1 L of solution ($\sim 1\%$ solution).
12. Hydroxylamine hydrochloride, $\text{NH}_2\text{OH} \cdot \text{HCl}$.

SAMPLE PREPARATION

A. Dry ashing

1. Weigh an aliquot of < 10 g vegetation into a tared 250-mL porcelain crucible. (**Note:** After ashing, several aliquots can be combined to provide adequate sample size.) Place each crucible in a muffle furnace with the crucible cover slightly ajar. Increase the temperature of the furnace at a rate of $0.80^{\circ}\text{C min}^{-1}$ to 250°C . Maintain this temperature for 30 minutes. Increase the temperature at a rate of $10^{\circ}\text{C min}^{-1}$ to 600°C . Maintain the temperature for 960 min to completely ash sample. Cool the crucible and weigh to determine percent ash. Ash content for replicate crucibles should vary by not more than 4%. If the ash content of an individual sample is lower by more than 4%, sample loss should be assumed and that sample discarded.
2. Place a known amount (approximately same amount as ^{241}Am in the sample) of ^{243}Am tracer (and/or ^{236}Pu tracer solution) in a 400-mL beaker containing a small amount of 1:1 HNO_3 . Transfer ashed vegetation to the beaker using 1:1 HNO_3 to dissolve the ash and rinse the crucible. Transfer as many aliquots to the beaker as needed to meet the detection requirements.
3. Cover with a watch glass and reflux on a hot plate until there is no evidence of remaining organic matter, adding HNO_3 or H_2O_2 as necessary.
4. Evaporate to near dryness. Add 50 mL 1:1 HNO_3 . Filter by gravity through a Whatman No. 42 filter paper, washing with 1:1 HNO_3 into a beaker. Continue with Step 5 below.

B. Wet ashing

1. Weigh an aliquot of vegetation into an appropriate sized beaker. (For a 100-300 g sample, use a 3000-mL beaker.) Add a known amount (approximately the same amount as expected of ^{241}Am in the sample) of ^{243}Am tracer solution (and/or ^{236}Pu tracer solution).
2. Slowly add 500 mL of 1:1 HNO_3 . Control the foaming, if necessary, with the addition of a few drops of n-octyl alcohol. Cover with a watch glass and place on a

low temperature hot plate overnight, maintaining a slow reaction and stirring as necessary to break up the foam. Gradually increase the temperature of the hot plate, adding HNO_3 and maintaining refluxing until the reaction is complete as indicated by the lack of brown nitrogen oxide gas.

3. Slowly add enough HCl to equal one third the volume of HNO_3 still in the beaker. Allow the mixture to react at room temperature for 15 min, cover with a watch glass, then heat on a low temperature hot plate overnight with occasional stirring.
4. Remove the sample from the hot plate, add an equal volume of water. Allow the sample to cool to room temperature. Filter by gravity through a large Whatman No. 42 filter paper into a beaker. Wash with 1:1 HNO_3 .
5. Retain the filtrate and evaporate to near dryness. Return the residue and filter to the original beaker. Add 100 mL HNO_3 , cover with a watch glass and place on a hotplate to reflux until colorless. Change the watch glass to a ribbed watch glass and evaporate to near dryness.
6. Transfer the digested filter with the residue to a 250-mL Teflon beaker using 1:1 HNO_3 . Evaporate to dryness. Add 15 mL of HNO_3 and 15 mL of HF to the beaker and evaporate to near dryness on a medium temperature hot plate. Repeat the addition of the HF/HNO_3 and the evaporation process two or three times.
7. Add 30 mL HNO_3 and evaporate to dryness, repeat twice, rinsing the walls of the beaker with acid. Add 20 mL HNO_3 . Add 20 mL of water. Cool. Filter by gravity through a Whatman No. 42 filter paper into the beaker with the filtrate from Step 5. Rinse with 1:1 HNO_3 .
8. Evaporate filtrate to dryness. Redissolve in 30 mL 1:1 HNO_3 . Proceed to Ion Exchange Purification for Plutonium Determination, Procedure Pu-11-RC, saving the column effluents for **Americium Determination**.

AMERICIUM DETERMINATION

1. Evaporate the americium containing effluents in a beaker to incipient dryness. Redissolve in a minimum amount (20-100 mL) of 1:1 HNO₃, dilute with four volumes of water.
2. Add 5 mL of calcium carrier solution (500 mg of calcium) and 50 g L⁻¹ of oxalic acid to the sample, while stirring with a magnetic stirrer. The total volume of the sample solution can be estimated using the markings on the beaker, and the amount of oxalic acid to be added is calculated using that volume.
3. Adjust the pH of the solution to 2.0 - 2.5 with NH₄OH using pH paper as an indicator and continue to stir for 30 min. Remove the magnetic stir bar.
4. Cool and let stand until precipitate settles and solution clears. Check for completeness of precipitation using a drop of saturated H₂C₂O₄ solution. Aspirate as much liquid as possible without disturbing the precipitate. Transfer precipitate to a 250-mL centrifuge bottle using oxalate wash solution (see **Note 3**). Balance the bottles on a double pan balance and centrifuge for 10 min at 2000 rpm. Discard the supernate.
5. Wash the precipitate with the oxalate wash solution. Centrifuge and discard the wash. Repeat wash. Redissolve the precipitate in a minimal amount (50-70 mL) of concentrated HCl. (**Note:** Dissolution is easier if the centrifuge bottle is placed in a hot water bath and stirred with a glass stirring rod.)
6. Transfer the precipitate to the original beaker. Add ~3 volumes of water, 50 g L⁻¹ of oxalic acid, and reprecipitate the oxalate with NH₄OH at a pH of 2.5-3.5 (see Step 3).
7. Cool the solution, aspirate, transfer to a centrifuge bottle, centrifuge, wash and redissolve the precipitate (repeat Steps 4 and 5).
8. Transfer the solution to original beaker. Add ~3 volumes of water, 50 g L⁻¹ of oxalic acid, and reprecipitate the oxalate at a pH of 2.5-3.5 with NH₄OH (see Step 3).

9. Cool the solution, aspirate, transfer to a centrifuge bottle, centrifuge, wash and redissolve the precipitate in ~200 mL of concentrated HNO_3 .
10. Transfer the solution to the original beaker and heat to destroy oxalate ion. Evaporate to near dryness. Dissolve in 1:1 HNO_3 and transfer to the centrifuge bottle.
11. Add enough water to make ~1M HNO_3 . Warm the solution in a 90° hot water bath and add 200 μL iron carrier solution (20 mg iron).
12. Adjust the pH of the solution to 8-9 with NH_4OH , while stirring with a glass rod. Leave the solution in a hot water bath to digest for 20 min.
13. Cool in a cold water bath, rinse and remove the glass rod. Balance the bottles on a double pan balance and centrifuge for 40 min at 2000 rpm.
14. Aspirate the supernate and discard. Add 10 mL of concentrated HCl to dissolve the $\text{Fe}(\text{OH})_3$ pellet, four drops of 30% H_2O_2 to get rid of any Mn, followed by 100 mL of water, and heat in the water bath for 30 min to get rid of excess H_2O_2 .
15. Reprecipitate, centrifuge and redissolve. Repeat Steps 12 to 14 three times. Reprecipitate, centrifuge and redissolve. The final precipitate should be dissolved in 1:1 HNO_3 .
16. Transfer to a 250-mL beaker, evaporate to dryness, add 20 mL 1:1 HNO_3 , and evaporate to dryness again.
17. Dissolve the residue in 40 mL 1:1 HNO_3 . Cool in an ice-water bath. Add 0.6-1.0 g $\text{NH}_2\text{OH}\cdot\text{HCl}$, dissolve, and let react for 15 min. Cover with a watch glass. Heat on a low temperature hot plate to decompose unreacted $\text{NH}_2\text{OH}\cdot\text{HCl}$, then bring to gentle boil for 1-2 min. Cool and pass the solution through a 1:1 HNO_3 ion-exchange column (see **Note 1**). Collect the effluent in a 400-mL beaker. Wash with 150 mL of 1:1 HNO_3 , and collect in the beaker.
18. Evaporate the sample in the 400-mL beaker to dryness and treat several times with concentrated HCl . Dissolve the residue in 30 mL HCl . Pass this solution through a

- concentrated HCl ion exchange column (see **Note 2**). Collect the effluent in a 250-mL beaker, and wash with 100 mL of HCl. Evaporate and proceed to microprecipitation if no residue is visible. If residue remains, continue with Step 19.
19. Evaporate to dryness transferring the sample to a 50-mL beaker when volume is sufficiently diminished. Add 10-mL HNO₃ and evaporate to dryness. Add 3 mL 0.5M Al(NO₃)₃ in 2M HNO₃ to each residue and heat very gently to dissolve.
 20. Prepare a TRU Resin column. Wash the resin with 15 mL 2M HNO₃, and discard the effluent.
 21. Load the sample (see Step 19) on the column. Drain to the top of the resin. Wash the beaker with 3 mL 0.5M Al(NO₃)₃ in 2M HNO₃ and add to the column. Discard the effluent.
 22. Rinse the column with 8 mL 2M HNO₃, followed by 8 mL 1M HNO₃, and discard the effluents.
 23. Elute the americium with three 3 mL aliquots of 0.025M HNO₃ into a 50-mL beaker.
 24. Evaporate eluate to dryness. Convert the residue to the chloride form by adding 3-4 mL HCl. Evaporate to dryness. Redissolve in HCl and evaporate two more times. Proceed to microprecipitation.

Notes:

1. Preparation of 1:1 HNO₃ Column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer 15 mL of wet settled Bio-Rad AG 1-X8 resin (100-200 mesh) to the column with deionized distilled water, and allow to settle. Place a second plug of glass wool on top of the resin, and with the stopcock open allow the H₂O level to reach the top of the upper plug. Pass 150 mL (or enough so that the effluent tests free of Cl⁻ ion) of 1:1 HNO₃ through the resin bed in three 50-mL portions, allowing the level of each to reach the top of the upper glass wool plug.
2. Preparation of HCl Column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer 10 mL of wet settled Bio-Rad AG 1-X4 resin (100-200 mesh)

with deionized water to the column, and allow to settle. Place a second plug of glass wool on top of the resin, and with the stopcock open allow the H₂O level to reach the top of the upper plug. Pass two 50-mL volumes of HCl through the resin bed and allow each to reach the top of the upper glass wool plug.

3. If a centrifuge is not available, centrifugation can be replaced by filtering and wet ashing the filter paper and precipitate in HNO₃.

MICROPRECIPITATION

See Microprecipitation Source Preparation for Alpha Spectrometry, Procedure G-03.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	25
Counter Background	(cps)	15x10 ⁻⁶
Yield	(%)	50
Blank	(cps)	-
LLD (400 min)	(mBq)	1
LLD (1000 min)	(mBq)	0.5
LLD (5000 min)	(mBq)	0.3

Iron

Fe-01-RC

IRON IN AQUEOUS SAMPLES - DUAL-DPM MODE LIQUID SCINTILLATION ANALYSIS

Contact Person(s) : Salvatore C. Scarpitta

APPLICATION

The procedure is intended for the determination of ^{55}Fe , which decays by electron capture, in spiked aqueous samples that contain various mixed alpha, beta and gamma emitting radionuclides. Beta emitting ^{59}Fe ($E_{\text{max}} = 0.475 \text{ MeV}$) is added to the samples as the yield determinant prior to FeOH_3 scavenging. Following two anion exchange separations that remove most interferences, the samples (as FePO_4) are counted in a commercially available liquid scintillation counter that is operated in the dual-dpm mode. A single count, in a calibrated instrument, provides the quench corrected activity concentrations of ^{55}Fe in a sample based on recovered ^{59}Fe (Scarpitta and Fisenne, 1996). The procedure is adapted from ASTM (1990) and is used in the EML Quality Assessment Program (QAP, Sanderson and Greenlaw, 1996).

SPECIAL APPARATUS

1. Disposable 3-mL polypropylene mini-columns (Catalog No.257.0119; Whatman Co., 5285 NE Elam Young Pkwy, Suite A-400, Hillsboro, OR 97124).
2. Liquid scintillation counter - Packard Tri-Carb 2250CA, Packard Instrument Co., Meridan, CT 06540, or equivalent.
3. 20-mL low K borosilicate glass vials.

4. Centrifuge and 40-mL plastic tubes.
5. Vortexer.

SPECIAL REAGENTS

1. Anion exchange resin, Bio-Rad AG1-X8 (50-100 mesh), see Specification 7.4 - 25 mL equilibrated with 125 mL 12M HCl and 25 mL equilibrated with 125 mL of 1:1 HNO₃.
2. Cerium carrier: 1 mg mL⁻¹ - CeCl in dilute HCl.
3. Cesium carrier: 1 mg mL⁻¹ - CsCl in dilute HCl.
4. Cobalt carrier: 1 mg mL⁻¹ - CoCl₂ in dilute HCl.
5. Iron carrier: 5 mg mL⁻¹ - FeCl₃ in dilute HCl.
6. Manganese carrier: 1 mg mL⁻¹ - MnCl₂ in dilute HCl.
7. Strontium carrier: 1 mg mL⁻¹ - SrNO₃ in dilute HCl.
8. Zinc carrier: 1 mg mL⁻¹ - ZnCl₂ in dilute HCl.
9. Insta-Gel-XF liquid scintillation cocktail - Packard Instrument Co., Downers Grove, IL.
10. 10M HCl - dissolve 833 mL HCl to 1 L water.
11. 6M HCl - dilute HCl 1:1 in water.
12. 4M HCl - dissolve 333 mL HCl to 1 L water.
13. 0.5M HCl - dissolve 42 mL HCl to 1 L water.
14. 0.01M HCl - dissolve 20 mL 0.5M HCl to 1 L water.

15. 8N HNO_3 - dilute concentrated HNO_3 1:1 with water.
16. Ammonium phosphate 0.5M - dissolve 66 g of $(\text{NH}_4)_2\text{HPO}_4$ into 1 L of water.
17. Ammonium hydroxide - concentrated.
18. Quenching agent (e.g., chloroform, nitromethane, carbon tetrachloride, etc.).

SEPARATION

1. Gravimetrically add 100 dpm of ^{59}Fe yield tracer and 1 mL of $5\text{ mg mL}^{-1}\text{ Fe}^{+3}$ carrier solution to the sample in a 40-mL plastic centrifuge tube. Add 100 dpm ^{59}Fe tracer and 5 mg of Fe^{+3} carrier to a 20-mL glass scintillation vial labeled "Fe-59 Reference Standard." Set the "Fe-59 Reference Standard" aside until Step 12. Prepare two reagent blanks using 40-mL plastic centrifuge tubes, each containing 5 mg of Fe^{+3} carrier but **without** ^{59}Fe tracer. Add 1 mL of NH_4OH to samples and blanks, only, until $\text{pH} > 10$ and $\text{Fe}(\text{OH})_3$ precipitate forms.
2. Centrifuge samples and blanks at 2000 rpm for 10 min. Decant and wash the precipitate with water.
3. Reconstitute the precipitate with 1 mL of HCl .
4. Add 1 mL each of carriers (1 mg mL^{-1}).
5. Prepare 3-mL columns using resin equilibrated in concentrated HCl . Tap columns to speed flow and to assure packing of the resin.
6. Pass solution through the column, flow rate should be $5\text{--}8\text{ mL min}^{-1}$.
7. Elute with 10 mL volumes of each of the following acids 10M HCl , 6M HCl , 4M HCl to remove Mn, Cs, Ce, Sr and Co. Collect the three eluates in the same 50-mL beaker and discard.

8. Replace the 50-mL beaker with a 20-mL glass scintillation vial. Elute the iron with exactly 10 mL of 0.01M HCl. The solution should be yellow. This fraction is used in Step 11.
9. Add 10 mL of concentrated HNO₃ to the eluted sample in Step 8 to make it 8N.
10. Prepare a second column with the resin equilibrated with 8N HNO₃. Place a clean 50-mL labeled beaker under the column.
11. Pass the eluate from the first column through the second column to retain uranium, plutonium and zinc. Wash with 5-10 mL of 8N HNO₃ until the yellow colored drops, indicative of Fe⁺³, are absent from the eluate.
12. Add 10 mL of 0.5M (NH₄)₂HPO₄ to the 20-mL scintillation vial containing the iron eluate, and add concentrated NH₄OH dropwise until the pH is about 3.0. Gently heat on a hot plate to completely precipitate iron as FePO₄. Repeat this step using the "Fe-59 Reference Standard."
13. Quantitatively transfer the sample to a 40 mL plastic centrifuge tube, decant and wash the precipitate with hot water.
14. Dissolve the precipitate in 1 mL of 0.5M HCl to obtain a clear solution. (**Note:** This step is necessary to reduce color quenching of the sample.) Transfer the solution to a clean 20-mL glass scintillation vial, washing the centrifuge tube with two 0.5-mL portions of 0.5M HCl. The total transferred volume should **not** exceed 3 mL of 0.5M HCl.
15. Dispense 15 mL of Insta-Gel-XF liquid scintillation cocktail to each vial, cap, and vortex for 20 sec. Wipe the external surface of each vial with an alcohol soaked tissue. Let the samples adapt in the dark in the refrigerated liquid scintillation counter for 15 min prior to counting.
16. Proceed to **Determination**

DETERMINATION

A. Instrument calibration.

1. Define the ^{55}Fe and ^{59}Fe spectral ranges or window settings first (see **Note 1**).
2. Obtain the net activity (cpm) in each window setting by subtracting the background from the activity in the sample.
3. Determine the counting efficiencies (cpm dpm⁻¹) for ^{55}Fe and ^{59}Fe from two efficiency quench calibration curves (see **Note 2**).
4. Prepare unquenched ^{55}Fe and ^{59}Fe standards in the same geometry as the analytical samples.
5. Set the energy regions for ^{55}Fe (Region A) and ^{59}Fe (Region B) using the guidance found in the applicable liquid scintillation counter manual.
6. Optimize the two energy regions (the figure of merit is a common way to optimize the regions of interest) using the guidance found in the operating manual. Alternatively, follow Steps 7 to 9.
7. Perform a spectrum analysis using the ^{55}Fe standard, and visually adjust the energy range of Region A (0-14 keV, ^{55}Fe) to maximize the count rate and to minimize the energy range. (**Note:** A balance between the count rate and the energy range should be obtained.)
8. Perform a spectrum analysis using the ^{59}Fe standard, and visually adjust the energy range of Region B (15-500 keV, ^{59}Fe) to maximize the count rate and to minimize the energy range. (**Note:** A balance between the count rate and the energy range should be obtained.)
9. Utilizing the full window, set a third region as Region C (0-2000 keV).

B. Counting efficiency as a function of quenching.

1. Establish the efficiency curves (efficiency vs. QIP) for ^{55}Fe and ^{59}Fe using the preset windows for each.
2. Check the efficiency curves annually and regenerate them if any major component of the instrumentation is replaced.
3. Check the liquid scintillation counter's stability first before running the standards and samples by counting the background and the ^3H and ^{14}C standards provided by the instrument manufacturer using the "SN" (system normalization) counting plug. (**Note:** The instrument software contains an appropriate spreadsheet program that compares the count rate of these standards with previously determined standard data according to criteria currently in use at EML.)

Notes:

1. Before counting samples and blanks, the appropriate window settings are determined for the two regions of interest (i.e., ^{55}Fe , ^{59}Fe). Steps 1 to 8 are performed once, after which the appropriate parameters are manually set in the liquid scintillation counting instrument.
2. The efficiency curve is a plot of the counting efficiency as a function of the quench index parameter (QIP). The QIP is determined internally by the instrument, using a $^{133\text{m}}\text{Ba}$ source, and is also known as the automatic external standardization (AES) number or the transformed spectral index of the external standard (t/SIE). A sample aliquot is prepared with a measured volume of a scintillation cocktail that is then placed in a programmed liquid scintillation analyzer, which is operated in the dual-dpm counting mode.

CALIBRATION

A. ^{55}Fe

1. Use a small volume (0.1 mL) of ^{55}Fe tracer solution that has sufficient activity (i.e., 1000 dpm) to give a counting error of less than 1% for a 15-min count.
2. Record tracer information (including volume, activity concentration, reference date, etc.). Pipette various volumes of a quenching agent (i.e., nitromethane) into separately

labeled vials to obtain a range of quenching from high to low efficiency. (**Note:** The following are examples of quenching agent volumes: 0.01, 0.02, 0.03, 0.04, 0.06, 0.08 mL).

3. Prepare a vial labeled “zero” that does **not** contain a quenching agent. (**Note:** Do not use deionized water to dilute the six aqueous quench standards to a volume consistent with the preparation of the sample set.)
4. Dispense enough scintillation cocktail into each glass vial to make up the final volumes that are consistent with the sample set to be analyzed (e.g., 15 mL).
5. Cap and vortex the labeled scintillation vials for 10 to 20 sec. Wipe clean the vials with ethanol and a paper towel, and refrigerate in the dark for at least 10 min.
6. Load the six aqueous quench standards from Step 2 into the counting rack with the first sample labeled as “zero.” Select the dual-dpm mode from the main program menu. Key in (a) the number of standards per set for ^{55}Fe , (b) the activity per sample (dpm), (c) the reference date of the standards as MM/DD/YY, (d) the half-life of $^{55}\text{Fe} = 23976 \text{ d}$, and (e) low-level count mode (optional).
7. Count the quench standards, typically for 15 min (or until 1% counting statistics are obtained), in the three regions selected on the liquid scintillation counter. Hit the F2 key to count the data set (the corresponding QIPs given by the instrument are automatically recorded).
8. The net count rate for each quench standard vial is calculated automatically by subtracting the prepared background (zero) count rate in Region A from the measured gross count rates in Region A.
9. The efficiency (Eff) is also determined automatically for each quenched sample in units of $\text{counts min}^{-1}/\text{disintegration min}^{-1}$ by dividing the net activity measured in count min^{-1} by the calculated activity added in dpm. Also, the uncertainty in the efficiency, sigma (Eff), for each vial should be estimated for each vial.
10. The efficiency curve is generated by the instrument which plots $\text{Ln}(\text{Eff})$ versus the QIP. Many liquid scintillations systems are equipped with programs to generate efficiency curves. (**Note:** To use these applications, the operating manual should be referenced.)

11. A least squares fit on the plot may be performed. The coefficients (a) and (b) or the equation

$$\text{Eff} = a \exp[b * \text{QIP}]$$

(obtained from the intercept $[\ln a]$ and the slope $[b]$), and the fitting coefficient, R^2 , should be recorded.

B. ^{59}Fe .

1. Perform the calibration for ^{59}Fe in an identical fashion to ^{55}Fe (Steps A.1 to A.11), except that a tracer solution of ^{59}Fe is used instead of ^{55}Fe , and count rates are measured in Region B rather than Region A.
2. Steps 6 and 7 of ^{55}Fe calibration above should be followed using 45 d as the half-life of ^{59}Fe .

PREPARATION OF LIQUID SCINTILLATION COUNTING VIALS

1. Mark the appropriate glass liquid scintillation vials with the sample identification on the cap.
2. Individually pipette a known amount (e.g., 2.0 - 5.0 mL) of each sample into the appropriate scintillation vials.
3. Dispense an appropriate amount (e.g., 15 mL) of the scintillation cocktail into each scintillation vial. A separate vial containing 2-5 mL of water serves as "background" (see **Note 1**).
4. Load the samples into the counting rack with the first sample being "zero" from Step A3, **Determination**.
5. Use the Packard Instrument counting protocol plug No. 1 which is delegated for $^{55}\text{Fe}/^{59}\text{Fe}$ counting.

6. Select the “use curve” option from the count mode menu under the dual-dpm mode when counting samples for ^{55}Fe .

Note:

1. Check the samples for phase separation. If phase separation is evident, solubilizing or complexing agents will be required to produce a stable solution.

CALCULATIONS

When using the “dual-isotope” counting mode, calculations are performed internally by the liquid scintillation software and the results are given in dpm.

REFERENCES

ASTM Designation: D-4922-89

Standard Test Method for Determination of Radioactive Fe in Water. ASTM Committee D19, 1916 Race Place, Philadelphia PA, 19103, March (1990).

DeFilippis, S.

“ ^{55}Fe and ^{59}Fe : A Qualitative Comparison of Four Methods to Liquid Scintillation Activity Analysis”

Radioactivity Radiochemistry, 2, 14-21 (1991).

Sanderson, C. G. and P. Greenlaw

“Semi-Annual Report of the Department of Energy, Office of Environmental Restoration and Waste Management, Quality Assessment Program”

USDOE Report EML-581, July (1996)

Scarpitta, S. C. and I. M. Fisenne

“Calibration of a Liquid Scintillation Counter for Alpha, Beta and Cerenkov Counting”

USDOE Report EML-583, July (1996)

Tritium

³H-01-RC

TRITIUM IN WATER - ACID ELECTROLYSIS
(see Volume II)

³H-02-RC

TRITIUM IN WATER - ALKALINE ELECTROLYSIS
(*see Volume II*)

³H-03-RC

ORGANICALLY LABELED TRITIUM - COMBUSTION PROCEDURE
(see Volume II)

³H-04-RC

TRITIUM IN WATER - LIQUID SCINTILLATION COUNTING

Contact Person(s) : Salvatore C. Scarpitta

APPLICATION

The procedure is used for the rapid determination of tritium by liquid scintillation (LS) spectrometry. It applies to all clear liquid samples and it can be completed in a short period (1 to 2 h) once efficiency curves have been established. The procedure is designed for a Tri-Carb 2250CA LS counter using Insta-Gel XF cocktail and it requires distillation of the samples so that they are free of salts and other interfering radionuclides.

The ³H spectral range or window setting is first defined. The counting efficiencies are then determined by using efficiency curves (quench curves). The efficiency curve is a plot of the counting efficiency as a function of the quench index parameter (QIP). The QIP is also known as the automatic external standardization (AES) number or the transformed spectral index of the external standard (tSIE). A sample aliquot is prepared with a measured volume of a scintillation cocktail that is then placed in a programmed LS counter for spectrum analysis.

SPECIAL APPARATUS

1. Packard Tri-Carb 2250-CA LS spectrometer
2. Low ⁴⁰K borosilicate glass scintillation vials
3. Glass distillation apparatus
4. Refrigerator

5. Tritium source - sealed 20-mL scintillation vial with cocktail.
6. Carbon-14 source - sealed 20-mL scintillation vial with cocktail.
7. Background source - sealed 20-mL scintillation vial with cocktail.
8. Glass containers - where ³H is of concern to minimize evaporative loss of water.

SPECIAL REAGENTS

1. Standardized solutions of ³H water
2. Insta-gel-XF or equivalent scintillation cocktail
3. 30% H₂O₂
4. Ethanol (95%)
5. Quenching agent - e.g., chloroform, nitromethane, carbon tetrachloride, nitric acid, etc. (**Note:** Some of the quenching agents listed are **highly** toxic and/or are carcinogens, e.g., carbon tetrachloride, and the safety of handling and disposal is the responsibility of the user.)

INTERFERENCES

1. Perform a ³H distillation if information more accurate than gross tritium is needed.
2. Reanalyze samples with excessively high count rates (e.g., > 1,000,000 counts min⁻¹) using less sample material. (**Note:** When using this procedure, the calculated ³H concentration may be higher than the actual concentration because of possible interferences from other low-energy beta emitters and the beta continuum of high-energy beta particles.)

3. Add several drops of 30% H₂O₂ to the vial to bleach the sample if quenching causes the efficiency to drop to one fourth of the highest efficiency. (**Note:** Deep color in the samples may cause severe quenching that will lower the counting efficiency.)

DETERMINATION

A. Window settings. (see Note 1)

1. Prepare unquenched ³H standards in the same geometry as the analytical samples. Set the energy regions for ³H (Region A) using the guidance found in the applicable LS counter manual.
2. Optimize the energy regions using the guidance found in the operating manual (the figure of merit is a common way to optimize the regions of interest). Follow Step 3 as an alternate.
3. Perform a spectrum analysis using the ³H standard, and visually adjust the energy range of Region A (0 to 19 keV, ³H) to maximize the count rate and minimize the energy range. A balance between the count rate and the energy range should be obtained (see Note 2).

Notes:

1. Determine the ³H window settings before counting the samples and backgrounds.
2. If the sample is not distilled there may be interference from low energy beta particles with the same energy as ³H, as well as from the beta continuum from high energy beta particles.

B. Efficiency as a function of quenching. (see Note)

1. Use a small volume (10-50 µL) of ³H tracer solution that has sufficient activity to give a counting error of < 1%. Prepare approximately 6-8 standards.

2. Record the tracer information (including volume, activity concentration, reference date, etc.). In order to obtain a range of quenching from high to low efficiency, pipette various volumes of the quenching agent (i.e., nitromethane) into vials, separately labeled. The following quenching agent volumes are presented as an example: 0, 0.01, 0.02, 0.03, 0.05, and 0.08 mL. (**Note: Do not** use deionized water to dilute the aqueous standard to a volume consistent with the sample set preparation.)
3. Dispense enough scintillation cocktail into each glass vial to make up the final volumes consistent with the sample set to be analyzed (e.g., 15 mL).
4. Cap and shake vigorously the scintillation vials for 10 to 20 sec. Wipe the vials clean with 95% ethanol and a paper towel. Refrigerate the vials for at least 10 min.
5. Check the stability and operational order of the LS counter before running the standards and the samples. This can be done by: counting the background, the ³H standard, and the ¹⁴C standard provided by the instrument manufacturer; using an appropriate spreadsheet program; and then comparing the count rate of these standards with previously determined standard data according to criteria currently in use.
6. Count a background sample (prepared similarly to the standards) and the ³H standards for 30 min (or until 1% counting statistics are obtained) in the regions selected on the LS counter. Record the corresponding energy regions given by the instrument.
7. Calculate the net count rate for each vial by subtracting the prepared background count rates in Region A from the measured gross count rates in Region A.
8. Determine the beta efficiency (Eff_β) for each vial in units of count per min/disintegrations per min by dividing the net activity measured in counts min⁻¹ by the calculated activity added in dpm. Also, estimate the uncertainty in the β -efficiency, ϵ -(Eff) for each vial.
9. Generate the β -efficiency curve by plotting $\text{Ln}(\text{Eff}_\beta)$ versus the QIP. (**Note:** Many LS counting systems are equipped with programs to generate efficiency curves. To use these applications, the operating manual should be referenced.)

10. Perform a least squares fit on the plot. Record the coefficients (a) and (b) for the equation $\text{Eff} = a \exp(b * \text{QIP})$ and the fitting coefficient, R. Obtain the QIP from the intercept $[\ln a]$ and the slope $[b]$.

Note: Establish efficiency curves (efficiency vs. QIP) by using artificially quenched standards. Check the efficiency curves annually and regenerate them if any major component of the instrumentation is replaced.

SAMPLE PREPARATION

1. Mark the sample identification on the appropriate scintillation vials with ink that is not removable using ethanol.
2. Pipette a known amount (e.g., 2.0 - 5.0 mL) of each sample into the appropriate scintillation vials.
3. Dispense an appropriate amount (e.g., 15 mL) of scintillation cocktail into each scintillation vial.
4. Secure the cap onto each of the scintillation vials, then shake the vials vigorously for 10 to 20 sec. Wipe each vial on the outside with a paper towel wet with ethanol to remove any fingerprints.
5. Refrigerate the samples for at least 10 min before counting. (**Note:** The samples may also need to be “dark adapted” to minimize the potential for delayed scintillations. This can be accomplished by postponing the start of counting for 10-15 min.)
6. Prepare a background sample in the same manner as the samples. A prepared background sample is one that is developed using stable compounds (e.g., dead water), and has a matrix as similar as possible to that of the samples being analyzed.

7. Count the sample for an appropriate time (e.g., 10 min) in the energy regions specified in **Determination**, Step 7. Record the QIPs given by the instrument. Return the samples to a well-ventilated area and store until disposal when the sample counts are completed.

CALCULATIONS

Perform the calculations internally with the LS software when using the DPM mode, or refer to EPA-600 4-80-032, Method 906.0 (Krieger and Whittaker, 1980).

REFERENCE

Krieger, H. L. and E. L. Whittaker

“Prescribed Procedures for Measurements of Radioactivity in Drinking Water”

U. S. Environmental Protection Agency EPA-600 4-80-032, Method 906.0, August (1980)

Lead

Pb-01-RC

**LEAD-210 IN BONE, FOOD, URINE,
FECES, BLOOD, AIR, AND WATER**

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure is applicable to samples of bone, food, urine, feces, blood, air, and water and is based on the solvent extraction of a lead bromide complex into Aliquat-336 (Petrow and Cover, 1965; Morse and Welford, 1971).

Lead-210 is isolated from most interferences. Its progeny ^{210}Bi is separated from ^{210}Pb , and the β activity is measured radiometrically after ingrowth.

SPECIAL APPARATUS

1. Atomic absorption (AA) spectrometer.
2. Aluminum foil - 7.2 mg cm^{-2} .
3. Rings and discs - see Specification 7.2.
4. Mylar film - see Specification 7.3.
5. Teflon filter holder.
6. Combination magnetic stirrer and hot plate.
7. Plastic scintillation phosphors - see Specification 7.9.

SPECIAL REAGENTS

1. Aliquat-336, methyltricapryl-ammonium chloride (Henkel Corporation, 2430 N. Huachuca Dr., Tucson, AZ 85745-1273), 3:7 in toluene and washed twice with an equal volume of 1.5M hydrobromic acid.
2. Hydrobromic acid 48%.
3. Hydrobromic acid 3.0M - 340 mL of 48% HBr L⁻¹ of water.
4. Hydrobromic acid 1.5M - 170 mL of 48% HBr L⁻¹ of water.
5. Hydrobromic acid 0.1M - 10 mL of 48% HBr L⁻¹ of water.
6. Toluene.
7. Standard Pb solution - 1000 µg mL⁻¹.
8. Lead carrier: 20 mg Pb mL⁻¹ - 32 g Pb(NO₃)₂ L⁻¹ in 1:19 HNO₃.
9. Bismuth carrier: 10 mg Bi mL⁻¹ - 23.2 g Bi(NO₃)₃·5 H₂O L⁻¹ in 1:19 HNO₃.

SAMPLE PREPARATION

A. Water.

1. To daily collections of 20 L of tap water add 100 mL of HNO₃ and evaporate to about 100 mL (see Note 1).
2. Add 100 mL of HNO₃ and transfer to a 400-mL beaker. Complete the destruction of organic material and evaporate to near dryness.
3. Add 50 mL of 10% HNO₃ to the beaker and warm to affect dissolution of any residue.

4. Cool the solution to room temperature and transfer the sample solution to a 100-mL volumetric flask. Bring the solution to volume with 10% HNO_3 .
5. Pipette 1 mL of sample solution into a 10-mL volumetric flask. Bring the solution to volume with 10% HNO_3 . Reserve this solution to determine the stable Pb content of the sample by AA spectrometry (see **Note 2**).
6. Return the sample solution in the 100-mL volumetric flask (Step 4) to the 400-mL beaker. Add 1 mL of Pb carrier and evaporate the solution to dryness.
7. Add 100 mL of 3M HBr to the sample beaker and warm the solution. Cool the solution to room temperature and proceed with the **Determination**.

B. Urine, blood, feces and air filters.

1. Measure 2-L of urine and transfer to a 3-L beaker. Place a measured volume of blood or 24 h fecal sample in a 1-L beaker. Place the air filter in a 600-mL beaker (see **Note 1**).
2. Destroy most of the organic material by carefully heating with HNO_3 . Hydrogen peroxide can be used to complete the oxidation of organic material (see **Note 3**).
3. Add 50-mL of 10% HNO_3 to the beaker and warm to affect dissolution of any residue.
4. Cool the solution to room temperature and transfer the sample solution to a 100-mL volumetric flask. Bring the solution to volume with 10% HNO_3 .
5. Pipette 1 mL of sample solution into a 10-mL volumetric flask. Bring the solution to volume with 10% HNO_3 . Reserve this solution to determine the stable Pb content of the sample by AA spectrometry (see **Note 2**).
6. Transfer the sample solution in the 100-mL volumetric flask (Step 4) to the 400-mL beaker. Add 1 mL of Pb carrier and evaporate the solution to dryness.

7. Add 100-mL of 3M HBr to the sample beaker and warm the solution. Cool the solution to room temperature and proceed with the **Determination**.

C. Bone (see **Note 4**)

1. Weigh 20 g of bone ash and transfer to a 400-mL beaker.
2. Dissolve the ash in about 80 mL of 3M HBr and warm to complete the dissolution.
3. Cool the solution to room temperature and transfer the sample solution to a 100-mL volumetric flask. Bring the solution to volume with 3M HBr.
4. Pipette 1 mL of sample solution into a 10-mL volumetric flask. Bring the solution to volume with 10% HNO₃. Reserve this solution to determine the stable Pb content of the sample by AA spectrometry (see **Note 2**).
5. Transfer the sample solution in the 100-mL volumetric flask (Step 3) to the 400-mL beaker and add 1 mL of Pb carrier.
6. Proceed with the **Determination**.

D. Food.

1. Depending upon food type, freeze drying should be used to remove excess water prior to wet ashing the sample (see **Note 1**).
2. Destroy most of the organic material by carefully heating with HNO₃. Hydrogen peroxide can be used to complete the oxidation of organic material (see **Note 3**).
3. Add 50 mL of 10% HNO₃ to the beaker and warm to affect dissolution of any residue.
4. Cool the solution to room temperature and transfer the sample solution to a 100-mL volumetric flask. Bring the solution to volume with 10% HNO₃.

5. Pipette 1 mL of sample solution into a 10-mL volumetric flask. Bring the solution to volume with 10% HNO₃. Reserve this solution to determine the stable Pb content of the sample by AA spectrometry (see **Note 2**).
6. Transfer the sample solution in the 100-mL volumetric flask (Step 3) to the 400-mL beaker. Add 1 mL of Pb carrier and evaporate the solution to dryness.
7. Add 100-mL of 3M HBr to the same beaker and warm the solution. Cool the solution to room temperature and proceed with the **Determination**.

Notes:

1. It is necessary to analyze reagent blanks with each batch of samples to correct the ²¹⁰Pb results.
2. The stable Pb content of some samples may be high enough to contribute a significant fraction to the total stable Pb measured by AA. This would result in an inflated estimate of the Pb carrier yield.
3. Hydrogen peroxide contains measurable and variable amounts of stable Pb and should be used sparingly.
4. It has been shown at this Laboratory that no ²¹⁰Pb loss occurs from bone dry ashed below 700°C (Fisenne, 1994). The absence of ²¹⁰Pb loss was determined for three bone types — ribs, vertebrae, and femur. It is the practice at EML to dry ash bones for ²¹⁰Pb analyses at 550°C.

DETERMINATION

1. Transfer the 3M HBr solution to a 250-mL separatory funnel containing 75 mL of Aliquat-336.
2. Shake for 30 sec. Let the phases separate and discard the aqueous (lower) phase.

3. Wash the organic phase three times with 50-mL portions of 0.1M HBr and discard all washes (lower phases).
4. Wash the organic phase twice with an equal volume of water. Transfer the washed organic phase to a suitable disposal container.
5. Combine the strip solutions in a 400-mL beaker and add 100 mL of HNO₃.
6. Wait for any reaction to subside and heat gently until the organic residue is destroyed. Evaporate the solution to ~ 10 mL.

A. First milking.

1. Transfer the sample to a 40-mL centrifuge tube with water. Add 1 mL of Bi carrier.
2. Adjust the pH of the sample to 8 with NH₄OH.
3. Stir the sample and heat in a hot water bath.
4. Cool and centrifuge the tube for 10 min. Decant and discard the supernate.
5. Dissolve the precipitate with five drops of HCl.
6. Add 40 mL of water and heat with constant stirring.
7. Cool and centrifuge for 10 min. Decant and reserve the supernate in a 250-mL beaker.
8. Repeat Steps 5-7 twice more, combining the supernates. Discard the precipitate. Record the time and date for ingrowth of ²¹⁰Bi.
9. Add 1 mL of Bi carrier and 3-5 mL of HCl to the combined supernates. Reduce the volume to <100 mL.
10. Cool, transfer to a 100-mL volumetric flask and bring to volume with 0.5N HCl.

11. Pipette 1 mL of sample into a 10-mL volumetric flask. Bring to volume with 0.5N HCl.
12. Measure the quantity of Pb in both the sample and the separated Pb fraction in the 10-mL volumetric flasks on an AA spectrometer at 283 μm . (The calibration curve should have a working range of 0-50 $\mu\text{g mL}^{-1}$.)
13. Subtract the Pb content of the dissolved sample and the reagent blank from the total Pb content determined in Step 12 to obtain the Pb carrier yield.
14. Allow 2-3 weeks for ingrowth of ^{210}Bi into the main portion of the sample (Step 10).

B. Second milking.

1. Transfer the solution from the 100-mL volumetric flask to a 250-mL beaker and evaporate to about 15 mL.
2. Transfer the sample to a 40-mL centrifuge tube and adjust the pH to 8 with NH_4OH . Centrifuge the tube for 10 min. Decant and discard the supernate.
3. Dissolve the precipitate with five drops of HCl and bring volume of sample to 30 mL with H_2O . (Record the time and date for decay of ^{210}Bi .)
4. Heat with constant stirring in a hot water bath. Cool and centrifuge the tube for 10 min. Reserve the supernate for additional ^{210}Pb analysis in a 150-mL beaker.
5. Dissolve the precipitate with five drops of HCl and dilute to 30 mL with water.
6. Heat in a hot water bath with constant stirring. Cool and centrifuge the tube for 10 min. Combine the supernate with that from Step 4.
7. Dissolve the precipitate with five drops of HCl. Stir and dilute to 30 mL with water.
8. Heat the tube in a hot water bath with constant stirring. Cool, filter with suction on a preweighed 2.4 cm Whatman No. 42 filter paper using a Teflon filter holder.

9. Wash the tube and the precipitate with water and alcohol. Dry the paper and precipitate for 30 min at 110°C in a drying oven.
10. Cool and reweigh the filter to determine weight of BiOCl precipitate.
11. Mount the filtered sample on a nylon ring and disc, covering the sample with aluminum foil (7.2 mg cm⁻²), a plastic scintillation phosphor and Mylar film.
12. Measure the ²¹⁰Bi on a low-level β-scintillation counter. (Record the time and date for decay of ²¹⁰Bi.)
13. Standardize the counter with a known amount of ²¹⁰Pb from which ²¹⁰Bi has been separated and prepared in the same way as the sample.

DATA PROCESSING AND ANALYSES

The ²¹⁰Pb activity of the sample is calculated using the following formula:

$$\text{Bq of } ^{210}\text{Pb} = \frac{R_s Y_1 Y_2 E}{GD}$$

where

R_s = net counting rate of the sample,

Y_1 = yield factor for Pb carrier,

Y_2 = yield factor for Bi carrier,

E = counter efficiency factor,

G = growth factor (growth of ²¹⁰Bi from first milking to final milking), and

D = decay factor (decay of ²¹⁰Bi from final milking to time of counting).

LOWER LIMIT OF DETECTION (LLD)

		A	B
Counter efficiency	(%)	35	-
Counter background	(cps)	0.005	-
Yield	(%)	80	80
LLD (400 min)	(Bq)	0.01	0.007
LLD (1000 min)	(Bq)	0.005	0.005

A = ^{210}Pb separation, ^{210}Bi ingrowth, ^{210}Bi separation.

B = ^{210}Bi separation only.

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Pb-02-RC

**DETERMINATION OF ^{210}Pb in BONE ASH BY
MEASUREMENT OF ^{210}Po**

Contact Person(s) : Isabel M. Fisenne

APPLICATION

The procedure has been tested for sample weights of up to 15 g of bone ash.

Lead-210 may be determined in bone samples which have been dry ashed at temperatures up to 700°C. The dry ashed bone samples should be stored for at least 2 y to allow build-up of ^{210}Po (Fisenne, 1994).

Lead, bismuth, polonium and calcium are separated from phosphate and radium as the oxalates. Lead, bismuth and polonium are separated from calcium as the sulfides. Polonium and bismuth are spontaneously deposited on a nickel disc from a weakly acid solution. The ^{210}Po is measured by alpha spectrometry and the chemical yield is determined with the alpha emitting tracer ^{209}Po .

Radium-226 is separated from the reserved oxalate supernate as the sulfate. The Ra.BaSO_4 is dissolved in alkaline EDTA and the chemical yield is determined with the gamma-emitting tracer ^{133}Ba . The ^{226}Ra is determined by the radon emanation method (see Procedure Ra-03-RC).

The total and unsupported ^{210}Pb activities are calculated from the ^{210}Po and ^{226}Ra measurements by application of the Bateman equations for the decay of this subseries of the Uranium Series (see Procedure 5.6).

SPECIAL APPARATUS

1. Nickel discs - 1.74 cm diameter by 0.06 cm thick, "commercial" pure nickel. Prior to use, degrease the disc. [**Note:** Silver or platinum discs may be used but must be cleaned and recycled. The nickel discs are discarded after measurement of the sample.]
2. Deposition cells - see Specification 7.16.
3. Mechanical stirrers.
4. Teflon stirring rods.
5. Alpha spectrometry system.
6. Radon bubblers - see Specification 7.7.
7. Polyethylene transfer pipettes - see Specification 7.11.

SPECIAL REAGENTS

1. Polonium-209 tracer solution - 1 Bq g⁻¹ of 1N HNO₃ solution.
2. Lead carrier: 20 mg Pb mL⁻¹ - 32 g Pb(NO₃)₂ L⁻¹ of 1N HNO₃.
3. Calcium carrier - solid calcium propionate. [**Note:** Calcium carrier is added only to the reagent blank. The ²¹⁰Po and ²²⁶Ra blank value must be established for each lot of calcium propionate salt prior to its use.]
4. Thioacetamide solution - 100 g CH₃CSNH₂ L⁻¹ of water.
5. Barium-133 tracer solution - 1x10⁴ Bq g⁻¹ of 1N HCl.
6. Barium carrier: 20 mg mL⁻¹ - 30.4 g BaCl₂ L⁻¹ of 1N HCl.

7. Ammonium acetate solution - 15 g NH_4OAc L^{-1} of water.
8. Acetic acid solution - 20 mL glacial HOAc L^{-1} of water.
9. Ammonium sulfate solution - 100 g $(\text{NH}_4)_2\text{SO}_4$ L^{-1} of water.
10. Aerosol OT solution - 0.1%.
11. EDTA solution - 300 g tetrasodium salt L^{-1} of water. Filter the solution through a glass fiber filter prior to use.
12. Monoethanolamine - 1:1 solution with water.

SAMPLE PREPARATION

1. Weigh 5 g of bone ash and transfer to a graduated 1500-mL beaker.
2. Add a weighed aliquot of ^{209}Po (about 0.05 g) and ^{133}Ba (about 0.1 g) tracer solutions and 1 mL of Pb carrier solution to the beaker. [**Note:** Add 2.5 g of calcium propionate to the reagent blank beaker. DO NOT ADD CALCIUM PROPIONATE TO THE BONE ASH SAMPLES.]

LEAD SEPARATION

1. Add 25 mL of HNO_3 and 1 mL of HClO_4 to the samples and reagent blank beakers. [**Note:** HClO_4 is not required for samples dry ashed at $\geq 500^\circ\text{C}$.]
2. Place the covered beakers on a medium hotplate. Swirl the beakers to dissolve the bone ash.
3. Evaporate the solution to dense HClO_4 fumes. Do not allow the sample to reach dryness.

4. Convert the sample to chloride form with five successive additions of 25 mL of HCl. Evaporate the solution to near dryness between additions.
5. Add 25 mL of HCl and swirl the beaker to dissolve most of the solids. Remove the beaker from the hotplate.
6. Dilute the solution to 1 L with water. Stir the solution with a stirring rod to dissolve any remaining solids.
7. Return the beaker to the hotplate and heat the solution for 10 min.
8. Using NH_4OH in a wash bottle, and stirring constantly, adjust the pH to about 1.5 to 2. At this point no permanent hydroxide flock should be present. Any hydroxide flock is dissolved with the addition of 6N HCL. [Note: The pH of the reagent blank is determined with pH paper.]
9. Weigh 5 g of solid oxalic acid and add to the sample with stirring. Continue heating the solution for 10 min.
10. Adjust the pH to 2.0 using NH_4OH and pH paper for both the sample and the reagent blank. Stir continuously.
11. Remove the sample from the hotplate. Remove and rinse the stirring rod with water. Allow the oxalate precipitate to settle overnight.
12. Decant the supernate into a 3-L beaker and reserve for **Radium Separation**.
13. Destroy the oxalates by evaporating with two successive 25-mL portions of HNO_3 . Do not allow the sample to reach dryness.
14. Convert the sample to the chloride form with five successive 25-mL portions of HCl.
15. Add 25 mL of HCl and swirl the beaker to dissolve most of the solids. Add a minimum amount of water to reach complete solution.

16. Remove the beaker from the hotplate and cool.
17. Transfer the solution with water to a 250-mL centrifuge bottle. Wash the beaker with water and transfer the washings to the centrifuge bottle. Stir the solution. The solution volume should be about 200 mL.
18. Place the centrifuge bottle in a 90°C hot water bath. Heat for 10 min.
19. Add 5 mL of thioacetamide solution to the sample. Stir and heat in the water bath for 1 or 2 min.
20. Remove the sample from the water bath. While stirring continuously, add NH_4OH to the sample until the black precipitate just persists.
21. Return the sample to the water bath for 1 h.
22. Remove the sample from the water bath. Remove the stirring rod and rinse with water.
23. Dry the outside of the centrifuge bottle. Place the bottle in a centrifuge cup. Tare a pair of samples on a double pan balance.
24. Place the tared samples in the centrifuge. Centrifuge the samples at 1800 rpm for 1 h.
25. Remove the samples from the centrifuge. Add 1 drop of Aerosol OT and decant the sample. Discard the supernate.
26. Add 2 mL of HCl to the sample and stir to break up the PbS precipitate. Place the sample in the water bath. Heat for 5 min.
27. Wash the walls of the bottle with 10 mL of water and heat for an additional 10 min.
28. Gravity filter the sample through a 12.5-cm diameter Whatman No. 42 paper into a prepared deposition cell.

29. Wash the centrifuge bottle with water and add the washing to the filter. Wash the filter with water. Discard the filter.
30. Place a cylindrical metal weight over the deposition cell. [**Note:** A 4-cm diameter by 4-cm height length of galvanized pipe will do.]
31. Place the weighted cell in an 80°C water bath. Lower the stirring motor with the Teflon rod in its chuck so that the rod is within 1 cm of the nickel disc.
32. Turn on the motor and stir for 4 h at maximum agitation without splashing. Add small quantities of 0.5N HCl to the cell, and water to the water bath to replace evaporative losses.
33. Turn off the motor and raise it to clear the stirring rod from the top of the cell. Remove the cell from the water bath.
34. Pour off the solution and discard. Rinse the cell successively with 0.5N HCl and water. Discard the rinsing.
35. Dismantle the cell and discard the bottle. Remove the nickel sample disc from the cap and rinse with ethanol.
36. Place the disc on a warm hotplate to dry.
37. Measure the disc in an alpha spectrometry system to determine the ^{209}Po yield and the ^{210}Po content of the sample. [**Note:** Record the deposition date so that decay corrections for the unsupported ^{210}Po can be made from separation date to measurement date.]

RADIUM SEPARATION

1. Evaporate the radium-bearing oxalate solution to dryness on a medium hotplate.

2. Remove the beaker from the hotplate and cool slightly. Add two successive 25-mL portions of HNO_3 . Heat to destroy the oxalate.
3. Convert the sample to the chloride form with five successive 25-mL portions of HCl .
4. Add 25 mL of HCl to the beaker and warm to dissolve most of the solids. Add about 50 mL of water and stir to dissolve the remaining solids.
5. Transfer the warm solution to a 250-mL centrifuge bottle. Wash the beaker with water, police and transfer the washing to the centrifuge bottle.
6. Dilute 1 mL of barium carrier to about 5 mL with water. Stir the sample thoroughly and continuously while adding the diluted carrier solution dropwise.
7. Place the centrifuge bottle in a hot water bath and warm the solution for about 5 min.
8. With constant stirring, slowly add NH_4OH until a dense white permanent hydroxide flock forms.
9. Dissolve the flock in a minimum of HCl . [**Note:** For the blank, adjust the pH from 1.5 to 2.0 using pH paper.]
10. Add 2 mL of NH_4OAc solution and 1 mL of dilute HOAc solution to the centrifuge bottle. Stir thoroughly and cool the bottle to room temperature in a water bath.
11. Add 1 mL of $(\text{NH}_4)_2\text{SO}_4$ solution to the bottle. Stir, remove the rod and rinse with water. Let the bottle stand at room temperature for 1 h.
12. Dry the outside of the centrifuge bottle. Place the bottle in a centrifuge cup. Tare a pair of samples on a double pan balance.
13. Place the tared samples in the centrifuge. Centrifuge the samples at 1800 rpm for 1 h.
14. Remove the samples from the centrifuge. Add one drop of Aerosol OT to the bottle. Carefully decant and discard the supernate.

15. Heat 5 mL of EDTA solution (300 g L^{-1}) for each sample in a hot water bath.
16. Break up the BaSO_4 precipitate with the stirring rod. Add 5 mL of warm EDTA solution and 1 mL of 1:1 monoethanolamine. Stir and heat for about 5 min.
17. Wash down the sides of the centrifuge bottle with about 10 mL of water. Continue heating the bottle for 15 min, stirring occasionally.
18. Gravity filter the solution through a 12.5-cm diameter Whatman No. 42 filter paper into a 30-mL polyethylene bottle.
19. Wash the centrifuge bottle and the filter paper with water. Discard the filter paper.
20. Dilute the sample to the same liquid level as the ^{133}Ba standard. The standard is prepared by diluting a known aliquot (about 0.1 g) of ^{133}Ba solution to 25 mL in a 30 mL polyethylene bottle.
21. Gamma count the standard and samples to determine the chemical yield of barium.
22. Transfer the solution to a radon bubbler.
23. Proceed with emanation procedure for ^{226}Ra (Ra-03-RC) to determine the radium content of the sample.

LOWER LIMIT OF DETECTION (LLD)*

		^{210}Po	^{226}Ra
Counter efficiency	(%)	30.	56.
Counter background	(cps)	$4 \times 10^{-5} \pm 0.7 \times 10^{-5}$	$2.8 \times 10^{-3} \pm 0.2 \times 10^{-3}$
Yield	(%)	85.	85.
Blank	(cps)	$3.5 \times 10^{-4} \pm 0.6 \times 10^{-4}$	$2.0 \times 10^{-2} \pm 0.8 \times 10^{-2}$
LLD (1000 min)	(mBq)	1.3	1.5
LLD (2500 min)	(mBq)	1.0	N/A

*Reagent blanks must be processed with every batch of samples.

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Env. Int. , 20, 627-632 (1994)

Polonium

Po-01-RC

POLONIUM IN WATER AND URINE

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure is applicable to water and urine (Hursh, 1958). Organic materials which can be converted to Cl^- solutions should also lend themselves to analysis by the procedure given. Reagent blanks must be analyzed along with the samples. [**Note:** It has been shown (Fellman et al., 1989) that urine samples must be wet ashed to release polonium from metabolically labeled organic compounds. The procedure has been modified to incorporate the destruction of organic matter.]

Polonium is quantitatively deposited on a nickel disc from a strong HCl solution. This is a very specific separation and therefore can be carried out while many other radionuclides are present in the sample.

The plated disc is α counted on a scintillation counter. It is also possible to use a ^{208}Po or ^{209}Po tracer and count on an α spectrometer to measure chemical yield and the activity of the sample.

SPECIAL APPARATUS

1. Nickel discs - made of 0.064-cm thick "commercial pure" nickel sheets. Discs are 2.2 cm in diameter with a 0.16-cm hole set 0.16 cm in from the edge. [**Note:** Coating the disc on one side with an acid resistant paint allows counting time to be cut in half.]

SAMPLE PREPARATION

A. Water.

1. To 1000 mL of tap water in a 1500-mL beaker, add 50 mL of HCl.
2. Evaporate to a volume of 20 mL and transfer to a 250-mL beaker. Add 100 mL of water and 100 mg of ascorbic acid.
3. Proceed to **Determination**.

B. Urine.

1. If the time between sample collection and analysis is much greater than 1 h, the urine samples should be preserved by adding 1 mg of sulfamic acid per mL of urine and storing in a refrigerator at 3°C.
2. Measure 100 mL of urine in a graduated cylinder and transfer to a 250-mL beaker. Rinse the graduated cylinder with 20 mL of 1:1 HNO₃ and add to the urine.
3. Evaporate the solution to near dryness and add 5 mL portions of HNO₃ to destroy organic matter.
4. Convert the sample to the Cl⁻ form by evaporating to near dryness with three successive 5-mL portions of HCl.
5. Add 20 mL of 1:1 HCl and 100 mg of ascorbic acid to the beaker.

DETERMINATION

1. Place the beaker in a constant temperature bath at 55°C.
2. Degrease a nickel disc by dipping in HNO₃, followed by dipping in HCl and rinsing in water. Repeat until the surfaces of the disc are bright and shiny.

3. Suspend the disc on a glass stirring hook in the solution and stir for 2.5 h at a speed giving maximum agitation without splashing.
4. Remove the disc, rinse the stirring rod and disc with water and let dry in air.
5. Alpha count each side of the disc. Subtract background from each count and sum the two net cps.
6. Standardize the counter with a known quantity of any α emitter on a metal disc. Natural U plated on a similar disc is a convenient standard.

LOWER LIMIT OF DETECTION (LLD)

		A	B	C
Counter Efficiency	(%)	50	50	25
Counter Background	(cps)	1.675×10^{-5}	1.67×10^{-5}	8.33×10^{-5}
Yield	(%)	70	70	70
Blank	(cps)	-	-	-
LLD (400 min)	(mBq)	0.5	0.33	1.5
LLD (1000 min)	(mBq)	0.33	0.17	1.0
LLD (5000 min)	(mBq)	0.17	0.10	0.5

A = alpha scintillation counter (both sides)

B = alpha scintillation counter (one side)

C = solid-state alpha spectrometer (one side)

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Hursh, J. B. (Editor)
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Po-02-RC

**POLONIUM IN WATER, VEGETATION,
SOIL, AND AIR FILTERS**

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure has been tested for water, vegetation, soil, and Dynaweb filters. Reagent blanks must be analyzed along with the samples.

Polonium is equilibrated with ^{208}Po or ^{209}Po tracer and isolated from most other elements by coprecipitation with lead sulfide. The sulfide precipitate is dissolved in weak HCl solution. Polonium is quantitatively deposited on a nickel disc. The deposition is very specific and can be carried out in the presence of other radionuclides.

The plated disc is counted on an α spectrometer to measure chemical yield and activity of the sample. The solution from the deposition may be retained and analyzed for ^{210}Pb .

SPECIAL APPARATUS

1. Nickel discs - 1.75 cm diameter x 0.06 cm thick "commercial pure" nickel. Degrease in acetone, dip in HCl and rinse with water.
2. Electrolytic cell - see Specification 7.16.
3. Teflon stirring rods.

SPECIAL REAGENTS

1. Standardized ^{208}Po or ^{209}Po tracer solution - about 2 Bq g^{-1} in a dispensing bottle.
2. Lead carrier solution: 10 mg Pb mL^{-1} - $15.98 \text{ g Pb(NO}_3)_2 \text{ L}^{-1}$ of 1:99 HNO_3 .
3. Thioacetamide solution - $100 \text{ g CH}_3\text{CSNH}_2 \text{ L}^{-1}$ of water.
4. Saturated ascorbic acid solution.

SAMPLE PREPARATION

A. Tap water.

1. Transfer 2.5 L of tap water to a 3-L beaker.
2. Add 50 mL of HNO_3 and 1 mL of Pb carrier solution. Add a weighed aliquot (30-80 mBq) of the ^{208}Po or ^{209}Po tracer solution.
3. Evaporate and add additional aliquots of tap water until a 10-L collection has been obtained. Evaporate gently to about 25 mL.
4. Transfer the solution to a 90-mL centrifuge tube with H_2O . Continue with **Determination.**

B. Vegetation.

1. Weigh 100 g of dried ($105\text{-}110^\circ\text{C}$) material into a 400-mL beaker.
2. Add 1 mL of Pb carrier solution and a weighed aliquot (30-80 mBq) of ^{208}Po or ^{209}Po tracer solution.
3. Add 100 mL of HNO_3 with magnetic stirring using a Teflon-coated bar. Digest with gentle heat and stirring for 1 h.

4. Reduce the volume of the solution to about 25 mL and transfer the solution to a 90-mL centrifuge tube with water. Continue with **Determination**.

C. Soil.

1. Weigh 1 to 5 g of soil into a 40-mL platinum dish. Add 1 mL of Pb carrier and a weighed aliquot (30-80 mBq) of ^{208}Po or ^{209}Po tracer solution.
2. Add 10 mL of HNO_3 and 10 mL of 48% HF. Heat on a medium hot plate. Repeat the additions of HNO_3 and HF until no further dissolution takes place.
3. Add 10 mL of HNO_3 and reduce the volume to about 5 mL.
4. If insoluble material remains, filter the slurry by gravity through a Whatman No. 42 filter paper into a 90-mL centrifuge tube. Wash the filter with hot water. Discard the residue. Continue with **Determination**.

C. Dynaweb filter.

1. To a 8.9 cm diameter or 1/4 of an 20.3 cm diameter Dynaweb filter in a 600-mL beaker, add 1 mL of lead carrier and a weighed aliquot (30-80 mBq) of ^{208}Po or ^{209}Po tracer solution.
2. Add 300 mL of HNO_3 and digest on a medium hot plate.
3. Evaporate to about 25 mL. If the solution is not clear, repeat the evaporation with additional HNO_3 .
4. Add about 200 mL of water to polymerize the Dynaweb material.
5. Filter with suction through a Millipore filter and wash with water. Discard the filter and polymerized Dynaweb material.
6. Transfer the filtrate back into the original beaker.

7. Reduce the volume to 25 mL. Repeat Steps 4-6 until the Dynaweb material is completely removed.
8. Transfer the solution to a 90-mL centrifuge tube. Continue with **Determination**.

DETERMINATION

1. Reduce the volume to about 5 mL in a steam bath. Add 50 mL of water.
2. Adjust the pH to 3.5-4 with NH_4OH . Add 5 mL of thioacetamide solution. Digest in a steam bath for 1 h.
3. Cool, centrifuge, and decant the supernate. Discard the supernate.
4. Dissolve the precipitate in 2 mL of HCl. Add 50 mL of water.
5. Adjust the pH to 3.5-4 with NH_4OH . Add 2 mL of thioacetamide solution. Digest in a steam bath for 1 h.
6. Cool, centrifuge, and decant the supernate. Discard the supernate.
7. Dissolve the precipitate in 1 mL of HCl. Dilute the solution to 25 mL with water.
8. Filter the solution by gravity through a Whatman No. 41 filter paper into a prepared deposition cell. Wash the filter with hot 0.5N HCl. Discard the filter.
9. Add 1 mL of saturated ascorbic acid solution to the cell.
10. Place the cell in an 80°C water bath.
11. Stir with a Teflon stirrer for 4 h at a speed giving maximum agitation without splashing. Occasional small additions of 0.5N HCl are necessary to make up for evaporation of the solution.

12. Remove the cell from the water bath and pour off the solution into a beaker. Reserve for ^{210}Pb determination if required.
13. Dismantle the cell, rinse the disc with water, then ethanol. Air dry the disc.
14. Place the disc on a warm hotplate to dry.
15. Count the disc on an α spectrometer to resolve the ^{208}Po or ^{209}Po tracer and ^{210}Po .

LOWER LIMIT OF DETECTION (LLD)

		A	B	C	D
Counter Efficiency	(%)	40	40	40	40
Counter Background	(cps)	8.33×10^{-5}	8.33×10^{-5}	8.33×10^{-5}	8.33×10^{-5}
Yield	(%)	80	75	60	60
Blank	(cps)	0.01	0.01	0.01	0.01
LLD (400 min)	(mBq)	1.5	2.0	2.0	2.0
LLD (1000 min)	(mBq)	1.0	1.3	1.3	1.3
LLD (5000 min)	(mBq)	0.4	0.6	0.6	0.6

Solid-state alpha spectrometer:

A = H_2O

B = Vegetation

C = Soil

D = Dynaweb filter

Plutonium

Pu-01-RC

PLUTONIUM IN AIR FILTERS

Contact Person(s) : Anna Berne

APPLICATION

This procedure is applicable to all types of air filters. However, if the filter is made of an organic polymer, it is advisable to first decompose the filter in a muffle furnace at 450°C overnight. Samples are then digested in concentrated HNO₃, after which the remaining residue and filter material are treated with HF.

SPECIAL APPARATUS

1. Muffle furnace.
2. Pyrex long stem fluted funnel with an inside diameter of 9.5 cm.

SPECIAL REAGENT

1. Plutonium-236 tracer - a standard solution containing ~0.15 Bq g⁻¹ in a dispensing bottle.

SAMPLE PREPARATION

1. Place the air filter in a 400-mL (or appropriate size) beaker.
2. Add a known amount (~ 0.05 Bq) of ²³⁶Pu tracer.

3. Add 150 mL of concentrated HNO_3 and 50 mL of concentrated HCl (or appropriate amounts based on air filter size), allow sample to react for about 1 h. Place the sample on a hot plate and cover with a watch glass. Heat the sample overnight on a low setting. Continue heating until the volume is ~100 mL.
4. Remove the sample from the hot plate, add 100 mL of water and let the sample cool to room temperature. Filter by gravity using a conical funnel with an 18.5 cm Whatman No. 42 filter paper. Wash with 50-75 mL of 1:1 HNO_3 . Collect the filtrate in a 250-mL beaker, evaporate the filtrate to near dryness, add ~35 mL 1:1 HNO_3 , and save. Cover the beaker with parafilm to prevent changes in the concentration of 1:1 HNO_3 .
5. Transfer the filter and residue to the original beaker and wet ash with 150-200 mL concentrated HNO_3 . Allow refluxing to occur on low heat. **Do not boil.** Evaporate to ~25-30 mL.
6. Transfer the filtered residue to a platinum dish or Teflon beaker. Add 10 mL of HF , 5 mL of HNO_3 , and evaporate to near dryness. Add 10 mL of HNO_3 and 10 mL of HF , then evaporate to near dryness again. Repeat the addition of HNO_3 and HF two more times. Wash the sides of the vessel three times with 1:1 HNO_3 , and evaporate to dryness after each addition.
7. Add 20 mL of 1:1 HNO_3 to sample.
8. Filter the sample into the beaker containing the filtrate from Step 4 by gravity filtration using a conical funnel with a 18.5 cm Whatman No. 40 or No. 42 filter paper. Wash with 1:1 HNO_3 (~ 20 mL).
9. Adjust sample volume to 100 mL with 1:1 HNO_3 .
10. Proceed to **Plutonium Purification - Ion Exchange Technique**, Procedure Pu-11-RC.

Pu-02-RC

PLUTONIUM IN SOIL SAMPLES

(see Volume II)

Pu-03-RC

PLUTONIUM IN SOIL RESIDUE - TOTAL DISSOLUTION METHOD

Contact Person(s) : Anna Berne

APPLICATION

This procedure is applicable to acid leached soils as well as unleached soils (Krey and Bogen, 1987).

The silica in the sample is removed by the formation of SiF_4 using HF. The remaining residue is fused with KF to decompose the complex silicates, followed by the addition of H_2SO_4 to distill the remaining SiF_4 . This procedure is followed by a pyrosulfate fusion, and finally, coprecipitation with BaSO_4 .

SPECIAL REAGENTS

1. Potassium fluoride.
2. Sodium sulfate.
3. Hydroxylamine hydrochloride.
4. 10% BaCl_2 solution - 10 g of BaCl_2 100 mL^{-1} of water.

SAMPLE PREPARATION

1. Using 100 mL of concentrated HNO_3 , wet ash the sample and filter the remaining sample from the leaching of the soil (Steps 2-6 of **Sample Preparation**, Procedure Pu-02-RC).

2. Evaporate the sample on a hot plate making sure the sample is completely dry.
3. Transfer the mixture to a tared plastic zip lock bag. Quantitatively remove the soil residue from the beaker. Reweigh the bag to determine the mass of the residue.
4. Break apart large aggregates by kneading the residue in the bag so that the mixture is homogeneous.
5. Weigh out 50 g of the soil residue and transfer to a 250-mL platinum crucible.
6. Add a known amount (~ 0.05 Bq or appropriate amount) of ^{236}Pu tracer.
7. Add 5 mL of 1:1 HNO_3 to wet the soil residue. Very slowly add 10 mL of concentrated HF, it may be necessary to add the HF dropwise. If excessive frothing occurs, wet the sample with 1:1 HNO_3 from a wash bottle.
8. Add an additional 10 mL of HF carefully. Heat the sample at low heat on a hot plate until no liquid remains.
9. When the sample is dry, add another 10 mL of HF. Heat the sample on a hot plate until the sample is dry.
10. Repeat Step 9 until at least a total of 100 mL of HF has been added and the sample no longer fumes. During the heating of the sample, the soil residue may move up the walls of the platinum crucible. If this occurs wash the walls with HF.
11. To insure the absence of HF, heat the crucible with a Meker burner until the crucible glows red.
12. Cool the sample and add 20 g of $\text{KF} \cdot 2\text{H}_2\text{O}$. Heat the sample on a hot plate, mixing with a Teflon stirrer.
13. Continue heating the sample until all the water has evaporated (so that no splattering occurs in the next step). It may be necessary to raise the temperature of the hot plate to assure drying.

14. Place the sample in a muffle furnace and heat at 950°C for 30 min.
15. Remove the crucible from the furnace and cool to room temperature.
16. Slowly add 35 mL of concentrated H_2SO_4 to the crucible on a hot plate at low heat. Heat the sample until the evolution of a small amount of SO_3 vapors occurs. After this step, continue heating for 5 min.
17. Cool and add 20 g of anhydrous Na_2SO_4 .
18. Place the crucible on a clay triangle mounted on a ring stand and heat the crucible gently with a Meker burner, minimizing bumping and frothing of the sample. Gradually raise the amount of heat while watching for frothing, until the molten mass is dissolved (a clear red color), at this point the temperature is $\sim 700^\circ\text{C}$. Remove the Meker burner and cool the crucible to room temperature. (**Caution:** This fusion is to be performed in a hood because SO_3 fumes are emitted.)
19. Flex the walls of the crucible to break apart the fused cake. Transfer the fused material to a 1500-mL beaker and add 200 mL of water to the crucible. Heat the crucible on a hot plate to dissolve any material in the crucible. Transfer the water wash to the 1500-mL beaker containing the fused material.
20. Perform three additional 200-mL washes of the crucible, each time transferring the solution to the 1500-mL beaker.
21. Add 100 mL of concentrated HCl , 1 g of $\text{NH}_2\text{OH}\cdot\text{HCl}$ to the 1500-mL beaker, which contains the fused material and water, and heat the solution to dissolve the fused material. Cover with a watch glass.
22. Continue to heat the solution until the boiling point is reached. Using a pipette add 5 mL of 10% BaCl_2 solution and continue boiling the sample for 5 min.
23. Cool to room temperature and filter the solution mixture by gravity through a 15-cm Whatman No. 42 filter paper using a conical funnel. Wash the beaker well with four 50-mL portions of H_2O . Transfer each H_2O wash to the funnel containing the filtered precipitate. Discard the filtrate.
24. Transfer the filter paper containing the BaSO_4 precipitate to a small platinum crucible (40 mL). Heat the crucible with a Meker burner to decompose the filter paper.

25. Add 5 g of anhydrous Na_2CO_3 to the crucible and mix the Na_2CO_3 with the BaSO_4 precipitate. Place the crucible in a muffle furnace at 850°C for 30 min.
26. Remove the crucible from the furnace, cool to room temperature, add 5 mL of water, and heat gently on a hot plate.
27. Transfer the salts and wash the solution into a 40-mL centrifuge tube using a minimum amount of H_2O to effect the transfer.
28. Centrifuge the sample and discard the supernatant.
29. Dissolve the precipitate in the centrifuge tube with 5 mL of 6M HCl. Transfer the solution mixture to a 100-mL Teflon beaker using 6M HCl. Also, wash the sides of the platinum crucible with 6M HCl to remove any remaining residue and transfer to the Teflon beaker.
30. Add 5 mL of concentrated HF, place the beaker on a hot plate and evaporate the sample to near dryness.
31. Cool, add 5 mL of 1:1 HNO_3 , and 5 mL of concentrated HF, heat on a hot plate and evaporate to near dryness.
32. Add 15 mL of 1:1 HNO_3 and evaporate to near dryness.
33. Repeat Step 32, three to five times, to remove any traces of HF.
34. Add 20 mL of 1:1 HNO_3 and heat gently for a few minutes. Remove the beaker from heat, filter mixture under reduced pressure using a 25-mm Millipore filter with a $0.45\text{-}\mu\text{m}$ pore size or by gravity filtration through a 15-cm Whatman No. 42 filter paper using a conical funnel.
35. Wash the Teflon beaker with 15 mL of 1:1 HNO_3 and transfer the wash to the filtered precipitate. Discard the precipitate. Proceed to Plutonium Purification - Ion Exchange Technique (see Procedure *Pu-11-RC*).

REFERENCE

Krey, P. W. and D. C. Bogen

"Determination of Acid Leachable and Total Plutonium in Large Samples"

J. of Radioanalytical and Nuclear Chemistry, 115, 335-355, December (1987)

Pu-04-RC

PLUTONIUM IN TISSUE
(see Volume II)

Pu-05-RC

PLUTONIUM IN TISSUE - SOLVENT EXTRACTION
(see Volume II)

Pu-06-RC

PLUTONIUM IN URINE
(see Volume II)

Pu-07-RC

PLUTONIUM IN LARGE URINE SAMPLES
(see Volume II)

Pu-08-RC

**PLUTONIUM IN VEGETATION AND TISSUE -
NITRIC/HYDROCHLORIC ACID METHOD**

(see Volume II)

Pu-09-RC

**PLUTONIUM IN VEGETATION AND TISSUE -
NITRIC/SULFURIC ACID METHOD**

(see Volume II)

Pu-10-RC

PLUTONIUM IN WATER

Contact Person(s) : Anna Berne

APPLICATION

This procedure is used for all types of water samples (i.e., sea water, lake water, tap water, etc.). If the sample contains suspended particulates, they must be removed by filtration. Large volume samples are analyzed after evaporation in an acidic medium.

The sample is heated in HNO_3 and then in 3:1 HNO_3 :HCl. The volume is then reduced to near dryness and finally the volume of the sample is adjusted with 1:1 HNO_3 . The sample is then ready to be purified by ion exchange separation (see Procedure Pu-11-RC).

SPECIAL REAGENT

1. ^{236}Pu tracer - a standard solution containing 0.2 Bq g^{-1} in a dispensing bottle. The purity of the tracer is measured by α spectrometry.

SAMPLE PREPARATION

1. Transfer 100-1000 mL of a H_2O sample to a beaker.
2. To the sample add $\sim 0.05 \text{ Bq}$ (or appropriate amount) of ^{236}Pu tracer.
3. Add an equal amount of concentrated HNO_3 , cover the beaker with a watch glass and place on a hot plate. Reflux the solution for 4-8 h.

4. Replace the watch glass with a ribbed watch glass and evaporate the solution to near dryness. When the volume is reduced to ~ 100 mL, allow the solution to cool to room temperature and transfer to an appropriate size beaker.
5. Continue evaporating the sample to near dryness. Cool, add 75 mL of concentrated HNO_3 and 25 mL of concentrated HCl . Cover with a watch glass. Allow to react for 30 min. Then place the sample on a hot plate and bring to a boil. After the solution has boiled for 30 min, reduce heat and continue heating overnight. Do not allow the sample to evaporate to dryness.
6. Remove the sample from the hot plate and add 100 mL of H_2O to the sample. Allow the sample to cool to room temperature and filter under reduced pressure using a Buchner funnel with a Whatman No. 42 filter paper.
7. Wash with 50 mL of 1:1 HNO_3 and then 50 mL of H_2O .
8. Transfer the filtrate to a 250-mL beaker, cover the beaker with a ribbed watch glass.
9. (**Note:** If the filter paper contains a moderate amount of precipitate, it must be treated with HF .) Transfer the filter paper containing the residue from the HNO_3/HCl digestion to a platinum dish. Place the platinum dish in a muffle furnace and heat at 100°C , raise the temperature by increments of 100°C every hour until a final temperature of 450°C is reached. Continue heating at this temperature overnight. Turn off the muffle furnace and let the sample in the platinum dish cool sufficiently to remove it from the furnace. Add 15 mL of 1:1 HNO_3 and 15 mL of concentrated HF . Heat the sample to near dryness.
10. Repeat Step 9 two times.
11. Add 20 mL of 1:1 HNO_3 to the sample and heat on a hot plate under a low setting until near dryness (to remove traces of HF).
12. Repeat Step 11 two times.
13. Add 20 mL of 1:1 HNO_3 to sample.

14. Using a conical funnel, filter the sample by gravity through an 18.5 cm Whatman No. 42 filter paper into a beaker containing the filtrate from Step 9. Wash well with 1:1 HNO_3 .
15. Reduce the volume of the solution to near dryness on a hot plate.
16. Adjust the volume to 100 mL by the addition of 1:1 HNO_3 .
17. Proceed to Plutonium Purification - Ion Exchange Technique, Procedure *Pu-11-RC*.

Pu-11-RC

PLUTONIUM PURIFICATION - ION EXCHANGE TECHNIQUE

Contact Person(s) : Anna Berne

APPLICATION

This procedure has been applied to the leachates derived from the plutonium sample preparation methods described in this Manual. Ion exchange chromatography is used to remove the large amounts of impurities contained in these leachates.

SPECIAL APPARATUS

Ion exchange columns - see Specifications 7.5 and 7.6.

SPECIAL REAGENTS

1. 1:1 HNO₃ - 500 mL HNO₃ diluted to 1 L.
2. Hydroxylamine hydrochloride - NH₂OH·HCl
3. 0.3M hydroxylamine hydrochloride-0.5M HNO₃ - 20.85 g of NH₂OH·HCl diluted to 1 L with 0.5M HNO₃.
4. Anion exchange resin - Bio-Rad AG 1-X8 (100-200 mesh, Cl⁻ form), see Specification 7.4

ION EXCHANGE SEPARATION

1. Cool the sample in an ice bath, add 1 g of $\text{NH}_2\text{OH}\cdot\text{HCl}$, stir, and let stand in an ice bath for 15 min. Remove the sample from the ice bath and heat to boiling on a hot plate with medium heat for 1-3 min. Cool the sample to room temperature.
2. Prepare the ion exchange resin column (see **Note**).
3. Pass the sample through the resin bed at a flow of $\sim 1 \text{ mL min}^{-1}$. Wash the beaker and the column with 30 mL 1:1 HNO_3 three times. Allow the liquid to flow until the level reaches the top of the resin bed prior to each wash. Reserve the sample and wash the effluent for ^{241}Am determination (or until yield has been determined as satisfactory).
4. Elute the plutonium with 10 mL of 0.5 M HNO_3 twice - then with 100 mL of 0.3M hydroxylamine hydrochloride - 0.5M HNO_3 into a 250-mL beaker. Discard the resin.
5. Slowly add 25-30 mL HNO_3 until effervescence begins, then place on a hot plate and evaporate the eluate to dryness.
6. Dissolve the residue in 30 mL of 1:1 HNO_3 and cool in an ice bath. Add 500-600 mg of $\text{NH}_2\text{OH}\cdot\text{HCl}$ and repeat Steps 1-3 using a small column (see Specification 7.6) for all samples.
7. Wash the resin with 100 mL of HCl (two 10-mL portions followed by two 40 mL portions). Wash the resin with two 10-mL portions, followed by one 40-mL portion 1:1 HNO_3 . Save the effluent until yield determination.
8. Repeat Steps 4 and 5. Discard the resin.
9. Convert the residue to the Cl^- form by adding 5 mL of HCl and evaporating to dryness three times at a low temperature.
10. See Procedure G-03 for microprecipitation for α spectrometry.

Note: Preparation of Columns

1. When preparing a large soil sample use a large column (Specification 7.5), otherwise use the column described in Specification 7.6.
2. Position a plug of glass wool in the base of the column so that no resin will drain out.
3. Add sufficient resin to form a resin bed of 10 cm in length. Wash the column with sufficient 1:1 HNO_3 to remove the Cl^- ion from the resin. Test the effluent with a dilute silver nitrate solution.

Pu-12-RC

PLUTONIUM AND/OR AMERICIUM IN SOIL OR SEDIMENTS

Contact Person(s) : Anna Berne

APPLICATION

This procedure is applicable to soils which contain plutonium and americium deposited from worldwide fallout and some nuclear activities. A total dissolution technique is required for some soil samples for plutonium determination.

Plutonium and americium isotopes are leached and equilibrated with ^{236}Pu and ^{243}Am tracers with nitric and hydrochloric acids from soil samples of up to 100 g in size. Plutonium is isolated and purified by ion exchange. Americium is collected with a calcium oxalate precipitation, isolated and purified by ion exchange. After source preparation by microprecipitation, the plutonium isotopes and americium are determined by alpha spectrometry.

SPECIAL APPARATUS

1. For microprecipitation, see Procedure G-03.
2. Ion-exchange columns - see Specification 7.5.

SPECIAL REAGENTS

1. Americium-243 tracer solution, $\sim 0.15 \text{ Bq g}^{-1}$ in a dispensing bottle.

2. Plutonium-236 (^{242}Pu can also be used) tracer solution, $\sim 0.20 \text{ Bq g}^{-1}$ in a dispensing bottle.
3. Bio-Rad AG 1-X8 resin (100-200 mesh) - see Specification 7.4.
4. Bio-Rad AG 1-X4 resin (100-200 mesh) - see Specification 7.4.
5. TEVA resin 2 mL ion extraction columns (Aliquat 336, methyltricapryl-ammonium chloride, Henkel Corporation, Tucson, AZ 85745-1273, on Amberchrom resin) or equivalent or can be prepared from TEVA resin, Eichrom Industries, 8205 Cass Ave. Suite 107, Darien, IL 60561) - place a plug of glass wool in the bottom of a 2 mL plastic transfer pipette (see Specification 7.7). Add slurried TEVA resin (0.5 g). Place additional glass wool on the top of the resin.
6. 2M ammonium thiocyanate in 0.1M formic acid solution - dissolve 152 g of NH_4SCN in ASTM Type 2 water, add 4.25 mL formic acid, and dilute to 1 L.
7. 1M ammonium thiocyanate in 0.1M formic acid - dissolve 76 g of NH_4SCN in ASTM Type 2 water, add 4.25 mL formic acid, and dilute to 1 L.
8. Calcium carrier solution, 100 mg mL^{-1} - dissolve 25 g CaCO_3 in a minimal amount of concentrated HNO_3 , and dilute to 100 mL.
9. Iron carrier, 100 mg mL^{-1} - slowly heat 100 g of iron powder in 500 mL of HCl until reaction ceases. Carefully and slowly add 100 mL of HNO_3 while stirring. Cool and dilute to 1 L.
10. Oxalate wash solution - dissolve 10 g of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) to make 1 L of solution ($\sim 1\%$ solution).
11. Hydroxylamine hydrochloride, $\text{NH}_2\text{OH} \cdot \text{HCl}$ - solid.

SAMPLE PREPARATION

1. Weigh 1-100 g of soil into an appropriate sized beaker. Add weighed amounts of ^{243}Am and ^{236}Pu tracers.
2. Slowly add 100 mL (**Note:** volumes are based on 100 g sample and should be adjusted if sample size is smaller) of HNO_3 to the beaker. Control the foaming with the addition of a few drops of n-octyl alcohol. Stir sample with a glass stir rod to mix sample and acid. When the reaction subsides, add 30 mL of HCl , and stir. Allow the mixture to react at room temperature, rinse and remove stir rod, cover with a watch glass, then reflux on a low temperature hot plate overnight. Remove from hot plate and cool.
3. Dilute the solution in the beaker with water to 1:1 HNO_3 and filter the solution with vacuum through 9 or 11 cm Whatman No. 42 filter paper on a Büchner funnel into a 1 L flask. Wash with 1:1 HNO_3 . Retain the filtrate in a 2-L beaker, evaporate the filtrate until salting out begins to occur. Return the residue and filter to the original beaker using HNO_3 to complete the transfer.
4. Add HNO_3 to the beaker to bring the volume added to 100 mL. Stir with a glass rod to mix sample and acid. Cover with a watch glass and heat until filter is wet ashed. Remove from the hotplate and cool. Add 30 mL of HCl to the beaker, cover with the watch glass, and heat on a low temperature hot plate for about 3 h with occasional stirring. Remove the beaker from the hot plate, and cool.
5. Repeat Step 3; dilute, filter and wash. Combine the filtrates. Return the residue and filter to the original beaker.
6. Repeat Step 4; wet ash filter and leach sample.
7. Repeat Step 3; dilute, filter and wash. Combine the three filtrates in a beaker. Discard the residue and filter paper.
8. Heat the filtrate with repeated 50-mL additions of HNO_3 , covering the sample with a watch glass and letting the sample reflux until all organic matter is decomposed. Evaporate the solution to incipient dryness. Redissolve in 50-200 mL of 1:1 HNO_3 .

If the solution is not clear, proceed to Step 9, otherwise go to **Plutonium Determination**.

9. If any siliceous matter is present, filter into a flask by gravity through a Whatman No. 42 filter paper. Wash the residue with 1:1 HNO_3 , and reserve the filtrate.
10. Transfer the filter paper with the residue to the original beaker and wet ash the paper with 100 mL of HNO_3 . Repeat wet ashing two or three times, then transfer the residue in the beaker into a 250-mL Teflon beaker, using 1:1 HNO_3 . Evaporate to dryness.
11. Add 5-25 mL of HF and 5-25 mL of HNO_3 to the beaker and evaporate on a medium temperature hot plate. Repeat the addition of the HF/ HNO_3 and the evaporation process two or three times. Rinse the walls of the Teflon beaker with 1:1 HNO_3 and evaporate, and repeat. Evaporate to dryness. Dissolve with 1:1 HNO_3 and evaporate to dryness.
12. Dissolve the residue in 1:1 HNO_3 and filter by gravity through a Whatman No. 42 filter paper. Add the filtrate to the solution from Step 9. Discard the filter and any residue. Heat the combined solution to incipient dryness. Redissolve in 50-200 mL 1:1 HNO_3 .

PLUTONIUM DETERMINATION

Proceed to Plutonium Purification Ion Exchange Technique Procedure *Pu-11-RC*. Save the column effluents for **Americium Determination**.

AMERICIUM DETERMINATION

1. Evaporate the americium effluents to incipient dryness. Redissolve in a minimum amount of 1:1 HNO_3 , dilute with four volumes of water.

2. Add 5 mL of calcium carrier solution (500 mg of calcium) and 50 g L⁻¹ of oxalic acid to the sample while stirring with a magnetic stirrer. (**Note:** The total volume of the sample solution can be estimated using the markings on the beaker, and the amount of oxalic acid to be added is calculated using that volume.)
3. Adjust the pH of the solution to 2.0-2.5 with NH₄OH using pH paper as an indicator and continue to stir for 30 min. Remove the magnetic stir bar.
4. Cool the sample and let it stand until precipitate settles and solution clears (for more than 6 h or overnight). Check for completeness of precipitation using a drop of saturated H₂C₂O₄ solution. Aspirate (or decant), using a disposable transfer pipette and suction, as much liquid as possible without disturbing the precipitate. Transfer the precipitate to a 250-mL centrifuge bottle using oxalate wash solution (see **Note 1**). Balance the bottles on a double pan balance and centrifuge for 10 min at 2000 rpm. Decant and discard the supernate.
5. Break up the precipitate with a stirring rod and wash the precipitate with the oxalate wash solution. Centrifuge, decant and discard the wash. Repeat wash. Redissolve the precipitate in a minimal amount (50-70 mL) of concentrated HCl (the final precipitate should be redissolved in ~200 mL of HNO₃, then proceed to Step 8 below). (**Note:** Dissolution is easier if the centrifuge bottle is placed in a hot water bath and stirred with a glass rod).
6. Transfer the dissolved precipitate to the original 600-mL beaker. Add enough water to make ~ 1M solution. Add 50 g L⁻¹ of oxalic acid.
7. Repeat Steps 3 through 6 until supernate is colorless.
8. Transfer the dissolved precipitate to the original beaker and heat to destroy the oxalate ion. Evaporate to near dryness. Dissolve in a minimum of 1:1 HNO₃. Transfer to centrifuge bottle using water to complete the transfer.
9. Add enough water to make ~1M HNO₃. Warm the solution in a 90° hot water bath and add 0.2 mL iron carrier solution (20 mg iron).

10. With the centrifuge bottle in the hot water bath adjacent to a hood, adjust the pH of the solution to 8-9 with NH_4OH while stirring with a glass rod. Allow the solution to digest in a hot water bath for 20 min.
11. Cool in a cold water bath, rinse, and remove the glass rod. Balance the bottles on a double pan balance and centrifuge for 40 min at 2000 rpm.
12. Decant (or aspirate) and discard the supernate. Add 10 mL concentrated HCl to dissolve the $\text{Fe}(\text{OH})_3$ pellet. Add four drops 30% H_2O_2 to oxidize any Mn present, followed by 100 mL of water and heat in the water bath for 30 min to get rid of excess H_2O_2 .
13. Repeat Steps 10 to 12 three times. Reprecipitate, centrifuge and redissolve. The final precipitate should be redissolved in HNO_3 .
14. Transfer to a 250-mL beaker, evaporate to dryness, add 20 mL HNO_3 , and evaporate to dryness again.
15. Dissolve the wet-ashed residue in 40 mL 1:1 HNO_3 . Cool in an ice-water bath. Add 0.6-1.0 g $\text{NH}_2\text{OH} \cdot \text{HCl}$, dissolve, and let react for 15 min. Cover with a watch glass. Heat on a low temperature hot plate to decompose unreacted $\text{NH}_2\text{OH} \cdot \text{HCl}$, then bring to gentle boil for 1-2 min. Cool and pass the solution through a 1:1 HNO_3 ion-exchange column (see **Note 2**). Collect the effluent in a 400-mL beaker. Wash the column with 150 mL of 1:1 HNO_3 and collect in the beaker.
16. Evaporate the sample in the 400-mL beaker to dryness. Convert to HCl by adding 20-30 mL of HCl at a time, heat to almost dryness, and repeat the HCl addition and evaporation at least three times. Evaporate again and dissolve the final residue in 30 mL of HCl . Pass this solution through a 12N HCl ion exchange column (see **Note 3**). Collect the effluent in a 250-mL beaker. Wash the column with 100 mL of HCl and collect in the 250-mL beaker.
17. Evaporate to dryness. Dissolve the residue in 10 mL 2M NH_4SCN in 0.1M formic acid.

18. Prepare a TEVA column. Equilibrate the resin by adding 3-4 mL 2M NH_4SCN in 0.1M formic acid. Drain to the top of the resin.
19. Transfer the sample to the column. Drain to the top of the resin.
20. Wash the column with 10 mL 1M NH_4SCN in 0.1M formic acid. Discard wash.
21. Elute the americium with 15 mL 2M HCl into a clean 100-mL beaker.
22. Add approximately 10 mL aqua regia to the sample. Gently decompose the thiocyanate solution under a heat lamp. Allow the solution to develop a purple color which will slowly disappear.
23. Heat the sample on a hot plate to near dryness. Dissolve the residue in 3 to 4 mL HNO_3 . Evaporate to dryness. Redissolve in HNO_3 and evaporate two more times.
24. Convert to HCl by addition of 3-4 mL HCl . Evaporate to dryness. Redissolve in HCl and evaporate two more times. Proceed to microprecipitation.

Notes:

1. If a centrifuge is not available, centrifugation can be replaced by filtering and wet ashing filter paper and precipitate in HNO_3 .
2. Preparation of 1:1 HNO_3 column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer with ASTM Type 2 water, 15 mL of wet settled Bio-Rad AG 1-X8 resin (100-200 mesh) to the column and allow it to settle. Place a second plug of glass wool on top of the resin, and with the stopcock open allow the water level to reach the top of the upper plug. Pass 150 mL (or enough so that the effluent tests free of Cl^- ion) of 1:1 HNO_3 through the resin bed in three 50-mL portions, allowing the level of each to reach the top of the upper glass wool plug.
3. Preparation of HCl column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer with ASTM Type 2 water, 10 mL of wet settled Bio-Rad AG 1-X4 resin (100-200 mesh) to the column and allow it to settle. Place a second plug of glass wool on top of the resin and with the stopcock open allow the water level to reach the top of the upper plug. Pass two 50-mL volumes of HCl through the resin bed and allow each to reach the top of the upper glass wool plug.

MICROPRECIPITATION

See Microprecipitation Source Preparation for Alpha Spectrometry, Procedure G-03.

AMERICIUM LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	25
Counter Background	(cps)	15×10^{-6}
Yield	(%)	50
Blank	(cps)	-
LLD (400 min)	(mBq)	1
LLD (1000 min)	(mBq)	0.5
LLD (5000 min)	(mBq)	0.3

PLUTONIUM LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	25
Counter Background	(cps)	2×10^{-5}
Yield	(%)	75
Blank	(cps)	-
LLD (400 min)	(mBq)	1
LLD (1000 min)	(mBq)	0.5
LLD (5000 min)	(mBq)	0.2

Radium

Ra-01-RC

RADIUM-226 IN BONE ASH

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure is applicable to bone ash only and has been adapted from Hallden et al. (1963).

The separated sample is measured by radon emanation. Only ^{226}Ra yields a radon progeny with suitable characteristics, so the method is specific. Most of the calcium, the alkali metals and phosphates are separated by coprecipitation of the radium as sulfate with barium carrier in a buffered solution. Further purification is obtained by repeating this step in the presence of undissolved BaSO_4 . The sulfate precipitate is dissolved in alkaline EDTA to prepare the emanating solution. The chemical yield of barium is determined with the γ -emitting tracer ^{133}Ba .

SPECIAL APPARATUS

Radon bubblers - see Specification 7.7.

SPECIAL REAGENTS

1. Barium-133 tracer solution - about 50 counts sec^{-1} per 0.1-g aliquot, prepared in 1:99 HCl.
2. Barium carrier solution (20 mg mL^{-1}) - 30.4 g $\text{BaCl}_2 \text{ L}^{-1}$ of 1:99 HCl.

3. Ammonium acetate solution - 15 g $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ (NH_4OAc) L^{-1} of water.
4. Acetic acid solution - 20 mL glacial $\text{CH}_3\text{CO}_2\text{H}$ (HOAc) L^{-1} of water.
5. Ammonium sulfate solution - 100 g $(\text{NH}_4)_2\text{SO}_4$ L^{-1} of water.
6. Aerosol OT solution - 0.1%.
7. EDTA solution - 300 g tetrasodium salt of EDTA L^{-1} of water.
8. EDTA wash solution - 1:9 dilution of EDTA solution.
9. Monoethanolamine - 1:1 (v/v) with water.

DETERMINATION

1. Weigh 10 g of bone ash into a 90-mL glass or 100-mL polycarbonate centrifuge tube. Add a weighed aliquot (about 0.1 g) of ^{133}Ba tracer solution, and 1 mL of barium carrier solution.
2. Add 20 mL of HCl (slowly at first to prevent foaming). Stir and warm in an 85°C water bath for about 5 min.
3. Add 10 mL of water. Add NH_4OH until a dense white permanent hydroxide flock forms (about 8-10 mL).
4. Dissolve the flock in HCl (about 4 mL is required).
5. Add 2 mL of NH_4OAc solution and 1 mL of HOAc solution. Cool in a water bath to room temperature.
6. Add 1 mL of $(\text{NH}_4)_2\text{SO}_4$ solution. Stir and let stand for 0.5 h.
7. Centrifuge at 2000 rpm for 1 h. Add one drop of 0.1% Aerosol OT. Decant carefully and discard the supernate.

8. Add 5 mL of HCl and warm in an 85°C water bath for 5 min. (Most of the BaSO₄ remains as a precipitate.)
9. Add 10 mL of water and then add NH₄OH until a permanent flock forms.
10. Dissolve the flock in HCl.
11. Add 2 mL of NH₄OAc solution and 1 mL of HOAc solution. Cool in a water bath to room temperature.
12. Add 1 mL of (NH₄)₂SO₄ solution. Stir and let stand for 0.5 h.
13. Centrifuge at 2000 rpm for 1 h. Add one drop of 0.1% Aerosol OT. Decant carefully and discard the supernate.
14. Heat a solution of EDTA (300 g L⁻¹) and an EDTA wash solution (30 g L⁻¹) in an 85°C water bath.
15. Break up the BaSO₄ precipitate with a stirring rod. Add 1 mL of 1:1 mono-ethanolamine and 5 mL of the hot EDTA solution and stir. Let stand for 5 min.
16. Wash down the sides of the tube with about 10 mL of the hot EDTA wash solution. Let the tube remain in the water bath for 15 min, stirring occasionally.
17. Gravity filter the hot solution through a 12.5 cm Whatman No. 41 filter paper into a 30 mL polyethylene bottle.
18. Wash the centrifuge tube and the filter paper with hot EDTA wash solution. Discard the paper and residue.
19. Dilute the sample to the same liquid level as the ¹³³Ba standard. The standard prepared by diluting a known aliquot (about 0.1 g) of ¹³³Ba solution to 25 mL in a 30 mL polyethylene bottle. Gamma count on a flat crystal to determine the chemical yield of barium.
20. Transfer the sample solution to a ²²²Rn bubbler.

21. De-emanate ^{222}Rn by bubbling with forming gas for about 10 min at $100\text{ cm}^3\text{ min}^{-1}$ as described in Radium - Emanation Procedure (see Ra-02-RC). Record the time as the starting time for ^{222}Rn buildup. Continue the analysis using the emanation technique.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	57.5
Counter Background	(cps)	0.0028
Yield	(%)	90
Blank	(cps)	0.0012
LLD (400 min)	(mBq)	3.3
LLD (1000 min)	(mBq)	1.7

*Reagent blanks must be analyzed with each set of samples.

REFERENCE

Hallden, N. A., I. M. Fisenne and J. H. Harley
"The Determination of Radium-226 in Human Bone"
Talanta, 10, 1223-1227 (1963)

Ra-02-RC

RADIUM-226 - EMANATION PROCEDURE

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure is specific and may be applied to almost any matrix which can be converted to a homogeneous solution.

Radium-226 in solution can be determined by de-emanating its ^{222}Rn into an ionization chamber or scintillation cell for measurement. The ^{222}Rn can be de-emanated by bubbling an inert gas through the solution, either after equilibrium has been established or after any known time period. Two half-lives, 7.65 days for example, give 75% of the maximum buildup.

SPECIAL APPARATUS

1. Radon measuring equipment are described in Radon-222 in Air and Breath Samples, Procedure Rn-01-RC, and in Fisenne and Keller (1985).
2. Radon bubblers - see Specification 7.7.

SAMPLE PREPARATION

1. The sample with barium carrier should be in homogeneous solution in a volume of 15-25 mL. The solution should be acidic with perchloric acid, neutral or in basic EDTA solution. Hydrochloric acid, NH_3 or other volatile materials must be absent.

2. Detailed preparation procedures for separation of Ra from sample matrices are presented in other radium procedures in this Manual.
3. Almost all types of samples require simultaneous analysis of reagent blanks, since radium appears in many chemical compounds. Using distilled or organic reagents reduces possible contamination.

DETERMINATION

1. Transfer the sample solution to a ^{222}Rn bubbler.
2. Clamp the bubbler in place to the ^{222}Rn system.
3. Open the forming gas (85% N_2 , 15% H_2) tank valve and adjust the line pressure to 70 kPa (10 psi) gauge.
4. Bleed the gas line, the rotometer, and 9.5 mm diameter rubber tubing.
5. Adjust the flow through the rotometer to a rate of $20 \text{ cm}^3 \text{ min}^{-1}$.
6. Open both stopcocks on the ^{222}Rn bubbler.
7. Attach the rubber tubing on the exit of the rotometer to the inlet of the ^{222}Rn bubbler. Adjust the forming gas flow rate through the bubbler to $100 \text{ cm}^3 \text{ min}^{-1}$.
8. Flush the ^{222}Rn from the solution (de-emanate) for 10 min.
9. Close both stopcocks simultaneously. Record the date and time as the beginning of the ^{222}Rn build-up period.
10. Shut off the forming gas and remove the rubber tubing from the bubbler.
11. Place the ^{222}Rn bubbler in a refrigerator for a suitable build-up period, usually 1 week.
12. To emanate ^{222}Rn into a pulse ionization chamber, repeat Steps 2-4.

13. Attach the rubber tubing from the rotometer to the inlet of the measurement system.
14. Open the valve to the ionization chamber and close the vacuum valves. Partially fill the chamber with forming gas to a pressure of -2.7 (-50 cm of Hg) gauge. Close the chamber valve and system entry valve. Open the vacuum valves and detach the rubber tubing from the measurement system.
15. Attach a small drying tube containing about 5 g of a color indicating drying agent and 4 cm lengths of 9.5 mm diameter rubber tubing at both ends to the outlet of the bubbler and the inlet of the measurement system.
16. Open the system entry valve to evacuate the drying tube for 3 min.
17. Adjust the forming gas flow rate to $20 \text{ cm}^3 \text{ min}^{-1}$ and attach the tubing outlet of the rotometer to the inlet of the bubbler.
18. Close the vacuum valves and open the ionization chamber valve.
19. Open the outlet stopcock of the bubbler and allow the bubbling to subside. Record the date and time as the end of the ^{222}Rn build-up period.
20. Carefully open the bubbler inlet stopcock and adjust the forming gas flow through the bubbler to about $100 \text{ cm}^3 \text{ min}^{-1}$.
21. When the system gauge indicates that atmospheric pressure has been reached, close both bubbler stopcocks simultaneously. Close the chamber, system entry and forming gas valves. Open the vacuum valves.
22. Remove the bubbler and drying tube from the system. Record the date and time of the end of the emanation as the beginning of the next ^{222}Rn build-up period.
23. Turn on the ionization chamber high voltage. A red LED will light when the chamber is at or above atmospheric pressure.
24. Measure the sample for at least 17 h.

Notes for Proper Operation:

1. If the Teflon stopcocks of the bubbler are snug fitting, it is not necessary to grease them. If they do leak, however, a silicone stopcock grease may be used.
2. The glass-to-glass ground joint at the top of the bubbler should also be lightly greased with silicone.
3. During the de-emanation, the gas bubbling should be started slowly to prevent popping of the bubbler top or stopcocks.
4. A better transfer of ^{222}Rn from acid or neutral solutions is obtained if the bubbler is first chilled in a refrigerator. This apparently reduces the bubble size and improves the transfer efficiency. For samples dissolved in alkaline EDTA solution, a drop of octyl alcohol is added to reduce foaming.

STANDARDIZATION

The chambers are standardized by de-emanating aliquots of a National Institute of Standards and Technology SRM ^{226}Ra solution contained in ^{222}Rn bubblers.

DATA PROCESSING AND ANALYSES

1. For routine work, discard the first 5 h of counting data (equilibrium for ^{222}Rn and progeny).
2. Determine the total count over the remaining counting period.
3. Calculate the net counts per hour per sample by determining the total sample counts per hour and subtracting the background counts per hour.
4. Divide the net counts per hour by the chamber standardization value of net counts per hour per Bq of ^{222}Rn .
5. Using the midpoint of the counting interval as the time of counting, extrapolate the value obtained to the time noted for the end of ^{222}Rn buildup. Figure 1 may be used for this calculation. This correction is only a few percent. The decay during the counting period is small and is not corrected for.

6. Correct the ^{222}Rn measurement at the end of buildup for the fractional buildup. The figure in Procedure Rn-01-RC may be used to obtain the build-up factor.
7. Subtract the value obtained by carrying a blank determination through the full procedure.
8. Samples are measured twice and the mean and standard deviation of the duplicate emanation results are reported.
9. A computational data sheet is attached for handling routine calculations on a step-by-step basis.

LOWER LIMIT OF DETECTION (LLD)*

Counter Efficiency	(%)	57.5
Counter Background	(cps)	0.0028
Yield	(%)	90
Blank	(cps)	0.0012
LLD (400 min)	(mBq)	3.3
LLD (1000 min)	(mBq)	1.7

*Reagent blank must be analyzed with each set of samples.

REFERENCE

Fisenne, I. M. and H. W. Keller

"The EML Pulse Ionization Chamber Systems for the Measurement of Radon-222"

USDOE Report EML-437, March (1985)

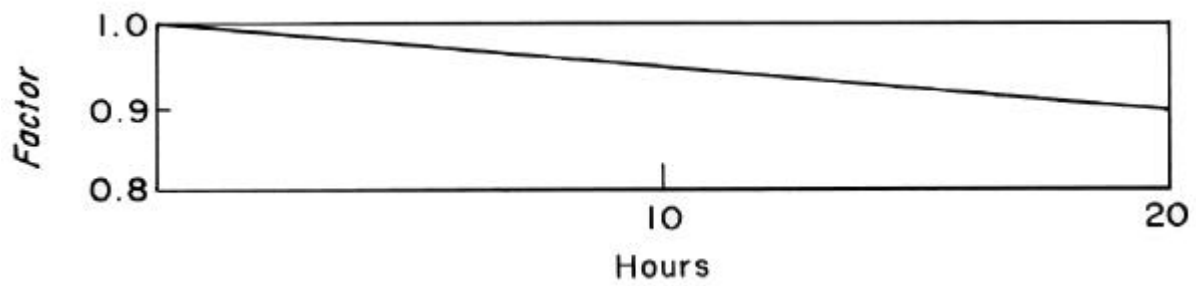


Figure 1. Correction factor from midpoint to the counting interval to the start of radon measurements interval.

Date _____

Sample Number

		Operation						
1	Chamber number	-						
	BACKGROUND							
2	Total count	-						
3	Count interval (h)	-						
4	Background (cph)	2/3						
	STANDARDIZATION							
5	Chamber factor cph Bq ⁻¹	-						
	SAMPLE COUNT							
6	Total count	-						
7	Count interval (h)	-						
8	Sample at count time (cph)	6/7						
	CORRECTIONS							
9	Time for midpoint of count	-						
10	Time for end of buildup	-						
11	Difference (days)	9-10						
12	Factor (from graph)	-						
13	Sample at end of buildup	8/12						

Date _____

Sample Number

		Operation						
14	Time for start of buildup	-						
15	Time for end of buildup	10						
16	Difference	15-14						
17	Factor (from graph)	-						
18	Sample with full buildup	13/17						
19	Bq in sample	18/5						
20	Bq in blank*							
21	Net Bq in sample	19-20						

*This sheet is suitable for calculating the blank value.

Ra-03-RC

**RADIUM-226 IN SOIL, VEGETATION ASH,
AND ION EXCHANGE RESIN**

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure is applicable to 5 g samples of soil and 10 g of vegetation ash or to ion exchange resin from sampling columns.

Soil, vegetation ash or ion exchange resin are prepared for ^{222}Rn emanation measurement. The sample is pretreated with HNO_3 -HF, fused with KF and transposed to pyrosulfate (Sill, 1961). The cake is dissolved in dilute HCl. RaBaSO_4 is precipitated, filtered, and dissolved in alkaline EDTA. The chemical yield is determined with the γ -emitting tracer ^{133}Ba .

SPECIAL APPARATUS

1. Radon bubblers - see Specification 7.7.
2. 100 mL platinum dishes or 250 mL platinum crucibles.
3. Millipore filter setup - 47 mm diameter.
4. Millipore filters - 47 mm diameter, 0.45 μm pore size.

SPECIAL REAGENTS

1. Barium-133 tracer solution - about 50 cps per 0.1-g aliquot, prepared in 1:99 HCl.
2. Barium carrier solution (20 mg mL^{-1}) - $30.4 \text{ g BaCl}_2 \text{ L}^{-1}$ in 1:99 HCl.
3. EDTA solution - 300 g tetrasodium salt of EDTA L^{-1} of water.
4. Triethanolamine - 1:1 in water.

SAMPLE PREPARATION

A. Soil and vegetation.

1. Weigh 5 g of soil or 10 g of vegetation ash into a 100-mL platinum dish. Add a weighed aliquot (about 0.1 g) of ^{133}Ba tracer solution and 1 mL of Ba carrier solution.
2. Slowly add 10 mL of HNO_3 and 10 mL of HF to the sample and evaporate on a hot plate to near dryness.
3. Continue the analysis as described below.

B. Ion exchange resin.

1. Transfer the resin and paper pulp from the collection column to a 250-mL platinum crucible. Dry under a heat lamp and ash at 500°C in a muffle furnace for 48 h.
2. To the cooled crucible, add a weighed aliquot (about 0.1 g) of ^{133}Ba tracer solution and 1 mL of barium carrier solution.
3. Continue the analysis as described below.

DETERMINATION

1. Weigh out 15 g of KF and add to the sample. Press the KF into the sample with a plastic spatula.

Caution - wear rubber gloves and safety glasses during Steps 2-5.

2. Fuse the sample over an air fed Meker burner, gradually increasing the temperature until a clear melt is obtained. Cool the melt.
3. Using a burette, slowly add 17.5 mL of H_2SO_4 to the melt. Heat the dish on a hot plate until a clear melt accompanied by dense fumes is obtained. Cool the melt.
4. Weigh out 10 g of Na_2SO_4 , add to the dish and fuse over the Meker burner until a clear melt accompanied by dense fumes is obtained. Cool the melt.
5. Transfer the cake to a 600 mL beaker containing 350 mL of hot water and 25 mL of HCl. Stir the solution to dissolve the cake. Cool for 1 h.
6. Filter the precipitate onto a 47 mm diameter, 0.45 μm pore size Millipore filter into a 1 L sidearm flask, police the beaker, and wash with water. Add the washing to the funnel. Discard the filtrate.
7. Using a strong stream of water from a wash bottle, transfer the precipitate from the filter into a 150 mL beaker. Discard the filter.
8. Add 5 mL of EDTA solution and 1 mL of 1:1 triethanolamine to the beaker. Heat on a warm hot plate for about 15 min, stirring occasionally. Reduce the sample volume to ~15 mL.
9. Gravity filter the warm solution through a Whatman No. 41 filter paper into a 30-mL polyethylene bottle.
10. Wash the beaker dish and filter with hot water. Discard the filter.

11. Dilute the sample to the same liquid level as a known aliquot (about 0.1 g) of the ^{133}Ba tracer solution and dilute to 25 mL in a 30 mL polyethylene bottle.
12. Gamma count the samples and standard to determine the chemical yield of barium.
13. Transfer the sample to a ^{222}Rn bubbler with water.
14. De-emanate ^{222}Rn by bubbling with forming gas for about 10 min at 100 mL min^{-1} as described in $^{226}\text{Radium}$ - Emanation Procedure (see Ra-03-RC). Record the time as the starting time for ^{222}Rn buildup. Continue the analysis by the emanation technique.

LOWER LIMIT OF DETECTION (LLD)*

Counter Efficiency	(%)	57.5
Counter Background	(cps)	0.0028
Yield	(%)	90
Blank	(cps)	0.0020
LLD (400 min)	(mBq)	3.3
LLD (1000 min)	(mBq)	1.7

*Reagent blanks must be analyzed with each set of samples.

REFERENCE

Sill, C. W.

"Decomposition of Refractory Silicates in Ultramicro Analysis"

Anal. Chem., 33, 1684 (1961)

Ra-04-RC

RADIUM-226 IN TAP WATER, URINE, AND FECES

Contact Person(s) : Isabel M. Fisenne

APPLICATION

The procedure presented has been applied to tap water, ashed urine, and feces samples. Only ^{226}Ra yields ^{222}Rn progeny that has suitable characteristics for detection by an emanation technique; therefore, the procedure is specific.

After sample preparation, radium is isolated from most other elements by coprecipitation with barium sulfate. Further purification is obtained by the removal of silica with HF and reprecipitation of the sulfate. The sulfate precipitate is dissolved in alkaline EDTA to prepare the emanating solution. The chemical yield of barium is determined with the γ -emitting tracer ^{133}Ba .

SPECIAL APPARATUS

Radon bubblers - see Specification 7.7.

SPECIAL REAGENT

1. Barium carrier solution - 20 mg mL^{-1} - 30.4 g $\text{BaCl}_2 \text{ L}^{-1}$ in 1:99 HCl.
2. Ammonium sulfate solution - 100 g $(\text{NH}_4)_2\text{SO}_4 \text{ L}^{-1}$ in water.
3. Aerosol OT solution - 0.1%.

4. EDTA solution - 300 g tetrasodium salt of EDTA L⁻¹ in water.
5. EDTA wash solution - 1:9 dilution of EDTA solution.
6. Ammonium acetate solution - 15 g L⁻¹ in water.
7. Acetic acid solution - 20 mL glacial acetic L⁻¹ in water.
8. Triethanolamine - 1:1 in water.

SAMPLE PREPARATION

A. Tap water.

1. Transfer two 0.5-L of tap water to a 3 L beaker.
2. Add 25 mL of HCl and 1 mL of barium carrier solution. Add a weighed aliquot (about 0.1 g) of the ¹³³Ba tracer solution.
3. Evaporate and add an additional two 0.5-L aliquots of tap water until a 10-L collection has been obtained. Evaporate gently to about 100 mL.
4. Transfer to a 400-mL beaker with water, policing the sides of the 3-L beaker thoroughly. Evaporate gently to about 100-mL.
5. Adjust the pH to 4 with 1:1 NH₄OH and proceed with **Determination**.

B. Urine.

1. Weigh an aliquot of ¹³³Ba tracer solution (about 0.1 g) into a 2-L beaker containing a small amount of water and 1 mL of barium carrier solution.
2. Add 1500 mL of urine, then 100 mL of HNO₃ and evaporate to about 1-L.
3. Slowly add 100-mL of HNO₃.

4. Repeat the evaporation and addition of acid until a total of 500-mL of HNO_3 has been added.
5. Evaporate to about 20 mL. Transfer to a 400-mL beaker with water.
6. Adjust the pH to 4 with 1:1 NH_4OH and proceed with Determination.

C. Feces ash.

1. Weigh 1 g of fecal ash into a 150-mL beaker. Add a weighed aliquot (about 0.1 g) of ^{133}Ba tracer solution and 1 mL of barium carrier solution.
2. Cover the ash with a small quantity of water and slowly add 10 mL of HNO_3 . Evaporate to a small volume on a medium hot plate.
3. Add about 25 mL of water. Add NH_4OH until a permanent hydroxide flock forms (3-5 mL).
4. Dissolve the flock in a few drops of HNO_3 .
5. Add 2 mL of NH_4Ac solution and 1 mL of acetic acid solution. Dilute to about 100-mL and proceed with **Determination**.

DETERMINATION

1. Add 1 mL of $(\text{NH}_4)_2\text{SO}_4$ solution and allow the sample to digest for 1 h at room temperature.
2. Filter by gravity on a 9 cm Whatman No. 42 filter paper. Wash the paper thoroughly with water. Discard the filtrate and washings.
3. Transfer the paper to a platinum dish. Dry the paper and then ash at 500°C for about 1 h.
4. Add 1 mL of H_2SO_4 and 2 mL of HF. Evaporate to SO_3 fumes.

5. Cool and transfer to a 90 mL centrifuge tube with water.
6. Police the dish and add the washings to the centrifuge tube.
7. Stir and let stand for 0.5 h.
8. Centrifuge at 2000 rpm for 1 h. Add one drop of 0.1% Aerosol OT. Decant carefully and discard the supernate.
9. Heat a solution of EDTA (300 g L^{-1} EDTA) in an 85°C water bath.
10. Break up the BaSO_4 precipitate with a stirring rod.
11. Add 1 mL of 1:1 triethanolamine and 5 mL of the hot EDTA solution, and stir. Wash down the sides of the tube with water.
12. Digest in the steam bath for 15 min, stirring occasionally.
13. Transfer the solution to a 30-mL polyethylene bottle.
14. Dilute the sample to the same liquid level as a known aliquot (about 0.1 g) of ^{133}Ba solution diluted to 25 mL in a 30 mL polyethylene bottle.
15. Gamma count samples and standard on a flat crystal to determine the chemical yield of barium.
16. Transfer the sample solution to a radon bubbler.
17. De-emanate radon by bubbling with forming gas for about 10 min at $100 \text{ mL}^{-1} \text{ min}$ as described in Procedure Ra-03-RC. Record the time as the starting time for the radon build-up period. Continue the analysis by the emanation technique.

LOWER LIMIT OF DETECTION (LLD)*

		A	B	C
Counter Efficiency	(%)	57.5	57.5	57.5
Counter Background	(cps)	0.0028	0.0028	0.0028
Yield	(%)	90	80	85
Blank	(cps)	0.0012	0.0020	0.0012
LLD (400 min)	(mBq)	0.33	0.45	0.39
LLD (1000 min)	(mBq)	0.17	0.29	0.15

*Reagent blanks must be analyzed with each set of samples.

Pulse ionization chamber:

A = Tap water

B = Urine

C = Feces

Ra-05-RC

RADIUM-224 IN URINE
(see Volume II)

Ra-06-RC

RADIUM-226 IN URINE AND WATER

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure is applicable to samples of urine and water. Small amounts of thorium are carried by the BaSO_4 and the method fails in the presence of ^{230}Th . Natural thorium does not interfere. Other α -emitting isotopes of radium also interfere.

Radium is initially separated from untreated water or urine by coprecipitation with calcium phosphate. Calcium and most other elements are removed by coprecipitation of radium on barium sulfate. Organic material is removed by ignition, silica is removed by volatilization with HF , and the radium-barium sulfate is reprecipitated.

Radium-226 in the barium sulfate precipitate is stored to allow the buildup of ^{222}Rn , ^{218}Po , and ^{214}Po . The equilibrated α activities are then measured with a scintillation counter. The instrument response is converted to Bq by application of corrections for counter background and efficiency and for self-absorption. Chemical recovery is measured gravimetrically and the ^{226}Ra activity is equivalent to one-fourth of the total Bq measured.

SPECIAL APPARATUS

1. Rings and discs - see Specification 7.2.
2. Teflon filter holders and filter funnels and sample mounts - see Specification 7.12.
3. Mylar film - see Specification 7.10.

SPECIAL REAGENTS

1. Barium carrier solution: 5 mg Ba mL⁻¹ - 9.51 g Ba(NO₃)₂ L⁻¹ of 1:99 HCl.

SAMPLE PREPARATION

A. Water.

1. Transfer 4 L of the sample to a 5 L stainless steel pot.
2. Add 1 mL of barium carrier solution and 4 mL of HNO₃.
3. Evaporate to near dryness, add additional aliquots of water and HNO₃, and continue until 50 L of sample have been treated.
4. Evaporate to about 100 mL, add 3-4 g of NH₄Ac, and adjust the pH to 5 with 1:1 NH₄OH.

B. Urine.

1. Transfer a measured volume of urine to a 250-mL centrifuge bottle and add 1 mL of barium carrier solution.
2. Add 2 mL of H₃PO₄. Adjust the pH to 9 with 1:1 NH₄OH. Stir, centrifuge, and discard the supernate.
3. Dissolve the precipitate with 10 mL of HNO₃. Dilute to about 100 mL with water.
4. Add 1 mL of H₃PO₄. Adjust the pH to 9 with 1:1 NH₄OH. Stir, centrifuge, and discard the supernate.
5. Dissolve the precipitate in a few mL of acetic acid and dilute to 100 mL with water. Adjust the pH to 5 with 1:1 NH₄OH.

DETERMINATION

1. Add 3-4 g of $(\text{NH}_4)_2\text{SO}_4$ with stirring. Digest for 12 h. Cool and filter by gravity on a 9 cm Whatman No. 42 filter paper. Wash with 0.5% H_2SO_4 . Discard the filtrate and washings.
2. Transfer the precipitate and filter to a platinum dish. Dry and ignite at 900°C .
3. Cool and add 2 mL of 1:1 H_2SO_4 and 5 mL of HF. Evaporate on a sand bath until SO_3 fumes appear.
4. Transfer the solution to a 40 mL, heavy walled centrifuge tube with 30 mL of H_2O and digest for 12 h. Centrifuge and discard the supernate.
5. Wash the precipitate with 10 mL of water. Centrifuge and discard the washings.
6. Slurry the precipitate with water and filter on a tared Whatman No. 42 filter paper.
7. Dry in an oven at about 150°C for at least 2 h.
8. Cool, weigh, and mount on a ring and disc with an α phosphor and Mylar.
9. Store for 30 days and count on an α -scintillation counter.

DATA PROCESSING AND ANALYSES

The ^{226}Ra disintegration rate is obtained from the counting rate of the equilibrated radium fraction through the following calculation:

$$\text{Bq} = R_s \text{ YTCE}$$

where R_s is the net counting rate of the sample, Y is the recovery factor, T is the self-absorption correction, E is the counter efficiency factor, and C is a theoretical conversion from total α activity to ^{226}Ra α activity.

Chemical recovery, Y, is obtained by weighing the final Ba sulfate precipitate. The calculation of the recovery factor is:

$$Y = \frac{x}{(w - t) f}$$

where x is the weight of barium added as carrier, w is the total weight of the final precipitate and filter paper, t is the weight of the filter paper, and f is the gravimetric factor which equals 0.588 mg barium per mg of barium sulfate.

Self-absorption correction, T, is used to normalize the self-absorption of the ^{226}Ra , ^{222}Rn , ^{218}Po , and ^{214}Po α activities in samples and standards to a common thickness (mg cm^{-2}). T is obtained by counting representative α emitters over the energy range of 4.8-8.8 MeV in precipitates of varying sample thicknesses. The correction is taken as the ratio of counting rates at an arbitrary minimum thickness to other thicknesses over the range of probable sample recoveries. Figure 1 is a typical composite plot of the correction obtained for ^{230}Th , ^{212}Pb , and ^{226}Ra activities for varying thicknesses of their oxalate, chromate, and sulfate derivatives, respectively.

Theoretical activity conversion factor, C, equals 0.25 after 30 days of buildup, when the three α -emitting progeny are in secular equilibrium with ^{226}Ra . However, the ratio of ^{226}Ra to total α activity at any time after the separation of radium may be calculated from the Bateman equation for buildup of ^{222}Rn .

Efficiency factor, E, is determined by α counting a known quantity of ^{226}Ra under sample conditions. The correction is taken as the ratio of the theoretical activity to the observed counting rate. The calculation is expressed as:

$$E = \frac{A}{R_s' T' C'}$$

where A is the theoretical activity of the standard, and R_s' is the net counting rate of the standard, T' is the self-absorption correction for the standard, and C' is the theoretical ratio of ^{226}Ra to total α activity in the standard.

An accompanying computational data sheet illustrates a procedure for routine calculation of ^{226}Ra activity rates. Experimental data are tabulated as they are derived and the calculations are performed on a step-by-step basis.

LOWER LIMIT OF DETECTION (LLD)*

Counter efficiency	(%)	50
Counter background	(cps)	1.67×10^{-5}
Yield	(%)	85
Blank	(cps)	1.67×10^3
LLD (400 min)	(mBq)	3
LLD (1000 min)	(mBq)	2

*Reagent blank must be analyzed with each set of samples.

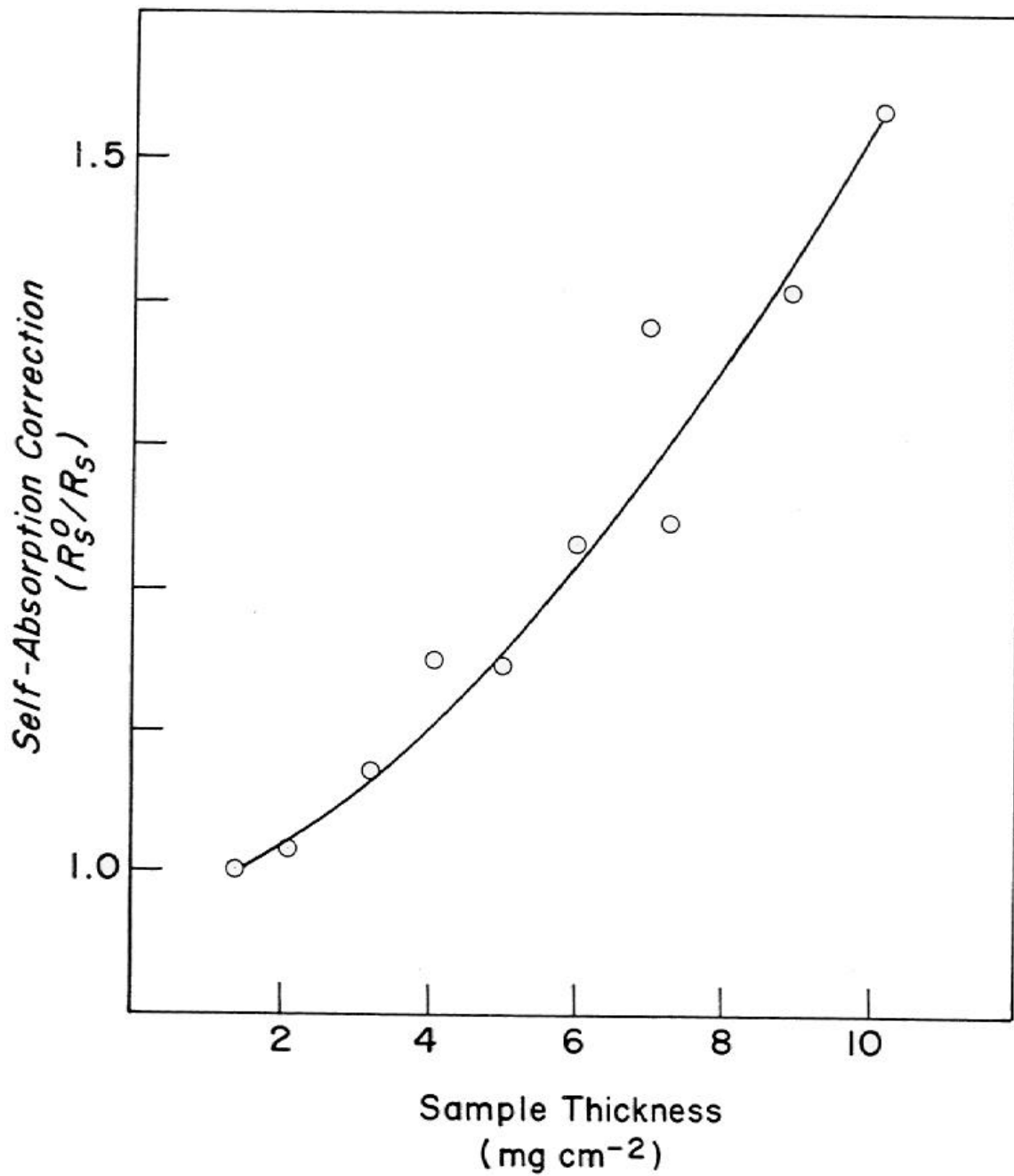


Figure 1. Self-absorption for α activities (4.8-8.9 MeV).

Date _____

Sample Number

		Operation						
1	Counter number	-						
	STANDARD							
2	Gross background count	-						
3	Count interval (s)	-						
4	Background (cps)	2/3						
5	Gross standard count	-						
6	Count time	-						
7	Standard (cps)	5/6						
8	Standard (net cps)	7-4						
	CORRECTIONS							
9	Gross weight (mg)	-						
10	Tare weight	-						
11	Net weight	9-10						
12	Weight of barium	11x0.59						
13	Carrier added	-						
14	Chemical yield factor (Y)	13/12						

Sample Number

[illegible]

Environmental Measurements Laboratory
U.S. Department of Energy

Date _____

Sample Number

		Operation						
1	Counter number	-						
3	Count interval (s)	Copy						
4	Background (cps)	Copy						
18	Efficiency factor (E)	Copy						
	SAMPLE COUNTING							
19	Gross sample count	-						
20	Count time	-						
21	Sample (cps)	19/20						
22	Sample (net cps)	21-4						
23	Sample (Bq)	22x18						
	CORRECTIONS							
24	Gross weight (mg)	-						
25	Tare weight	-						
26	Net weight	24-25						
27	Weight of barium	26x0.59						
28	Carrier added	-						
29	Chemical yield factor (Y)	28/27						
26	Net weight	Copy						
30	Thickness correction (T)	Graph						

Date _____

Sample Number

		Operation						
31	Corrected sample (Bq)	23x29x30						
	STANDARD							
32	Background/count interval	4/3						
33	Sample/count intervals (cps)	21/20						
34	S ²	32+33						
35	S for sample (net cps)	√34						
36	Total correction factor	18x29x30						
37	S for sample (Bq)	35x36						

Radon

Rn-01-RC

RADON-222 IN AIR AND BREATH SAMPLES

Contact Person(s) : Isabel M. Fisenne

APPLICATION

Procedures are presented which describe EML's method of sampling, counting, and calculating ^{222}Rn concentration in air and breath samples. When radium is present in the body, the gaseous progeny, ^{222}Rn ($t_{1/2} = 3.825$ d), will collect in the lungs and will be eliminated with exhaled breath.

One liter glass sampling flasks are provided to field personnel by EML for collecting breath or atmospheric ^{222}Rn samples. The ^{222}Rn sample is transferred to a pulse type ionization chamber, and after it is allowed to come into equilibrium with its progeny products, the sample is α counted. Two of the progeny, ^{218}Po and ^{214}Po , are α emitters and contribute to the total count.

SPECIAL APPARATUS

A. Sampling.

1. 1-L glass flasks with two large bore stopcocks per flask.
2. Tank of compressed, aged air with two-stage regulator.
3. Face mask - No. CS-6772 inhalator, modified to block the emergency intake and with the outlet modified to accept 9.5 mm ID rubber tubing (Mine Safety Appliance Co., Pittsburgh, PA).

4. Demand regulator - No. CS-46516 single stage or equivalent (Mine Safety Appliance Co., Pittsburgh, PA).

B. Analysis.

1. Platinum black catalyst (Baker and Co., Deoxo Units).
2. Drying tube with Drierite.
3. Flame arresters.
4. Capillary orifice.
5. Vacuum pump.
6. Tank of H₂ with two-stage regulator.
7. Tank of forming gas (85% N₂, 15% H₂) with two-stage regulator.
8. Sample introduction system including valves and piping.
9. Pulse type ionization chamber and associated electronic equipment.

SAMPLE COLLECTION

A. Radon in breath*

1. Set up the equipment as described in the above reference using 9.5 mm (3/8 in) rubber tubing on the inhalator outlet. Do not attach to sampling flask.
2. Clean facepiece with cotton and alcohol.
3. Set air pressure on two-stage regulator to 4.5 kg (10 lb).

* Taken from Harley *et al.*, 1951.

4. Have the subject hold the facepiece in place while you check for leaks, particularly around the bridge of the nose.
5. Have the subject breathe with the respirator for 5 min to flush the environmental air from his or her lungs. (This should be regular breathing. Do not ask for deep breaths.)
6. While the subject continues regular breathing, attach the sampling flask (with both stopcocks open) for a 1-min period, remove, and close stopcocks.
7. Repeat Step 6 for a duplicate sample.

B. Radon in the atmosphere.

1. Open both flask stopcocks.
2. Connect about 0.6 m of 9.5 mm (3/8 in) rubber tubing to one stopcock.
3. Inhale through the tubing and flask 20 times. Do not exhale through the flask. If convenient, a suction pump may be used.
4. Close both stopcocks.

MEASUREMENT EQUIPMENT PREPARATION

A. Sample oxidation.

Before transfer to the counting system, enough H_2 is added to the sample flask to completely remove O_2 (as H_2O) in the platinum catalyst. Because O_2 acts to quench the ionization produced by each α disintegration, even small amounts of it in the chamber will seriously affect the counting rate of a sample. Environmental air contains about 20% O_2 and the addition of 40 kPa (6 psi) of H_2 is theoretically sufficient for all samples. It has been our practice to add an excess of H_2 and therefore 70 kPa (10 psi) is usually added to each sample.

B. Flame arresters.

The removal of O_2 from the sample takes place in the platinum black catalyst where O_2 and H_2 combine to form H_2O . This combustion reaction generates a considerable amount of heat, and if allowed to strike back, the sample flask may explode. To prevent such explosions, flame arresters are placed between the catalyst and the sample. The flame arresters consist of a fine mesh copper wire screen and act to dissipate the heat of the reaction.

C. Capillary orifice.

A capillary orifice is placed in the line after the catalyst. This slows the passage of gas through the catalyst and insures complete combustion.

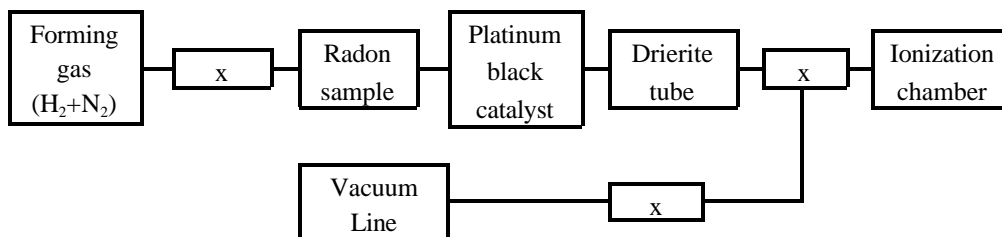
D. Drierite tube.

Water formed in the O_2 removal is collected in a Drierite tube. The Drierite is kept free of H_2O by evacuating the external piping of the system continuously when not transferring the samples.

E. Counting apparatus.

The ^{222}Rn counting apparatus consists of a sample introduction system, ionization chamber, preamplifier, amplifier, and count registering device. The ionization chamber counts almost 100% of the α disintegrations of ^{222}Rn and about 50% of the disintegrations of its progeny. Each chamber plus its sample introduction system has a capacity of 2 L and the chamber is operated at a potential of 1000 V. A mixture of H_2 (15%) and N_2 (85%) is used as a counting gas. The chambers are constructed of a specially selected, electropolished stainless steel and have a background count of about 10 counts h^{-1} and an efficiency of about 6215 counts h^{-1} for 1 Bq of ^{222}Rn .

A block diagram of the counting system and external apparatus is shown below.



x indicates valve or stopcock.

The pulses from the ionization chamber are fed to an EML-built preamplifier, amplifier, and control unit. Two Tattletale Clever counters are interfaced to a PC.

DETERMINATION

1. Connect sample flask to H₂ tank with 9.5 mm (3/8 in) rubber tubing.
2. Raise gauge pressure to 70 kPa (10 psi) gauge.
3. Open flask stopcock to tank to admit H₂ to the flask.
4. Close stopcock and tank valve.
5. Raise the forming gas line pressure to 70 kPa (10 psi) gauge and bleed the line and rubber tubing leading to sample inlet.
6. Connect one flask stopcock to the forming gas line with the above rubber tubing, the other to the counting system with another section of 9.5 mm (3/8 in) rubber tubing.
7. Open the ionization chamber and the vacuum line valve to evacuate the counting chamber, external piping, and the rubber tubing between the counting system and the flask.
8. Close the vacuum line valve when system reaches minus 10.1 kPa of Hg gauge pressure.

9. Open the flask stopcock to allow the sample to enter the counting system. Allow pressure equilibration (indicated by pressure gauge).
10. Check platinum catalyst by touch to assure that combination of H_2 and O_2 has occurred.
11. Close the flask stopcock to the counting system.
12. Open the stopcock to the forming gas line. Allow forming gas to come to pressure in the flask.
13. Repeat Steps 5 and 7 until the gauge indicates atmospheric pressure.
14. Open the stopcock to the forming gas line, then attach the stopcock to the counting system. Allow forming gas to flow until the gauge pressure reaches 35 kPa (5 psi).
15. Close all valves and remove flask and tubing from system.
16. Turn on ionization chamber high voltage.
17. Count the sample for at least 14 h.

DATA PROCESSING AND ANALYSES

1. Discard the first 5 h of counting data (equilibration period for ^{222}Rn and progeny).
2. Determine the gross count over the remaining counting period.
3. Calculate net counts per hour per sample by determining gross sample counts per hour and subtracting background counts per hour.
4. Divide net counts per hour by the chamber standardization value of net counts per hour per Bq of ^{222}Rn .

5. Using the midpoint of the counting interval as the time of counting, extrapolate the value obtained to the time of sampling. Figure 1 may be used for this calculation.

STANDARDIZATION

Each unit is standardized several times a year with ^{222}Rn from a radium solution obtained from the National Institute of Standard and Technology (NIST). This solution is diluted and split into aliquots which are placed in ^{222}Rn bubblers (see Specification 7.8). The ^{222}Rn is allowed to build up for a known period before the standard is used.

The ^{222}Rn standard is transferred to the chamber by emanation. The bubbler is first attached to the external feed system. When the ionization chamber and external system are evacuated, the vacuum line is shut off from the system and the bubbler outlet stopcock opened. The inlet stopcock is then opened and forming gas flushes the ^{222}Rn into the chamber until the system is brought to atmospheric pressure.

At equilibrium, there are three α disintegrations per ^{222}Rn disintegration, however, two of these are from the particulate α -emitting progeny. Since these α disintegrations deposit on the walls of the ionization chamber, they are counted with a maximum efficiency of 50%. One becquerel of ^{222}Rn in the ionization chamber thus has a theoretical counting rate of 7190 counts h^{-1} . Actually, the ionization chambers in this Laboratory yield a counting rate of 6215 counts h^{-1} Bq^{-1} of ^{222}Rn in equilibrium with its progeny or an overall efficiency of 86%.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	57.5
Counter Background	(cps)	0.0028
Yield	(%)	-
Blank	(cps)	-
LLD (400 min)	(Bq)	0.01
LLD (1000 min)	(Bq)	0.07

REFERENCE

Harley, J. H., E. Jetter and M. Eisenbud
"A Method of Obtaining Reproducible Breath Radon Samples"
Arch. Ind. Hyg. Occ. Med., 4, 1-9 (1951)

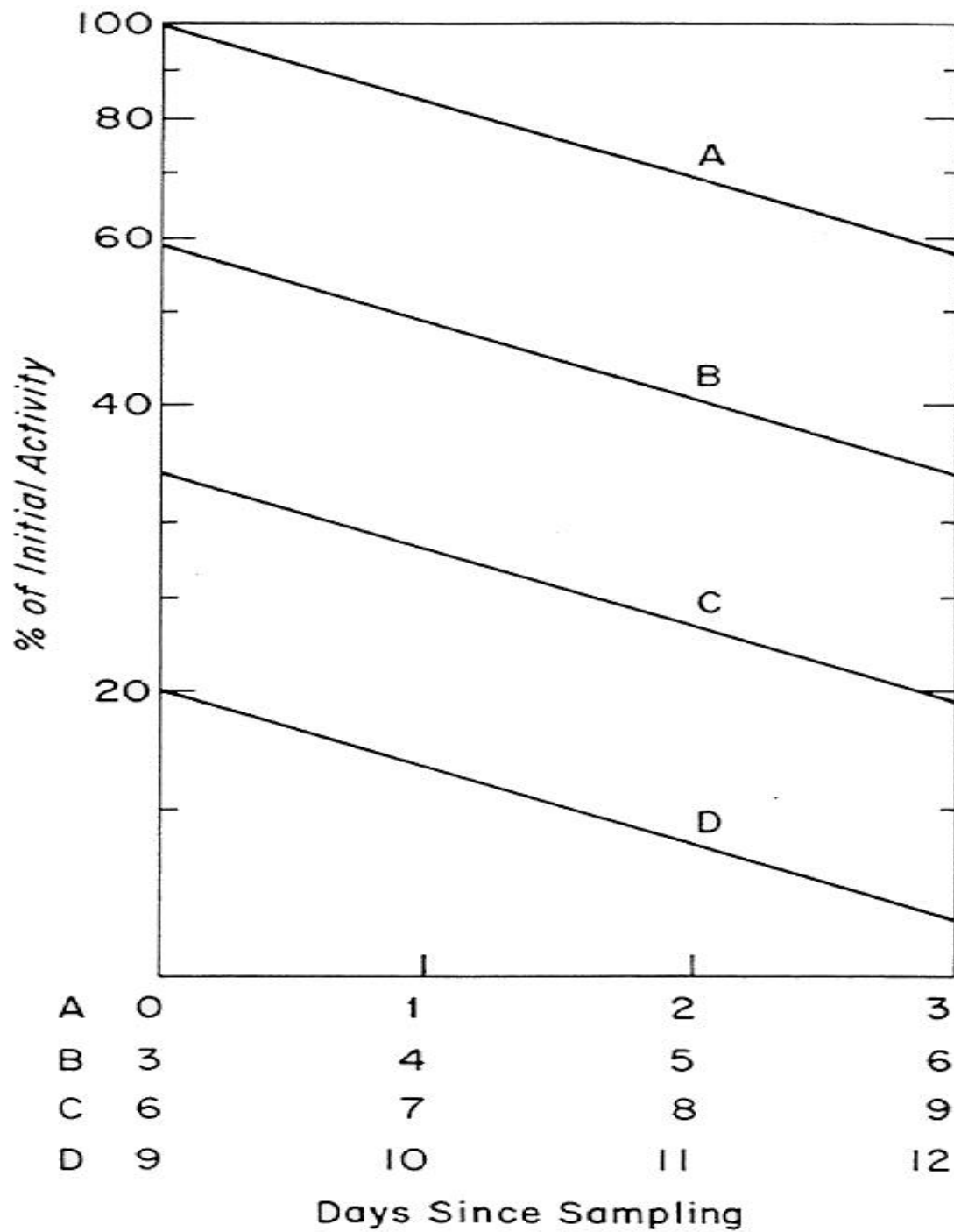


Figure 1. Decay correction for radon from the midpoint of the counting interval to collection time.

Strontium

Sr-01-RC

STRONTIUM-89
(see Volume II)

Sr-02-RC

STRONTIUM-90
(see Volume II)

Sr-03-RC

STRONTIUM-90 IN ENVIRONMENTAL MATRICES

Contact Person : Marie Lawrence

APPLICATION

This procedure is applicable to the preparation, separation, and analysis of vegetation, water, air filters and soil.

Strontium is separated from calcium, other fission products and natural radioactive elements. Fuming HNO_3 separations remove the calcium and most of the other interfering ions. Radium, lead and barium are removed with barium chromate. Traces of other fission products are scavenged with iron hydroxide. After the $^{90}\text{Sr} + ^{90}\text{Y}$ equilibrium has been attained, the ^{90}Y is precipitated as the hydroxide and converted to the oxalate for counting on a low-background gas proportional beta counter. Chemical yield is determined with ^{85}Sr tracer by counting in a gamma well detector.

SPECIAL APPARATUS

1. Teflon filter holder or filter funnel and sample mount - see Specification 7.12.
2. Rings and discs - see Specification 7.2.
3. Magnetic stirrers with Teflon-coated magnet bars.
4. Mylar film - see Specification 7.3.
5. Glass fiber filters - see Specification 7.8.
6. Fisher filtrator, Fisher Chemical Company, Pittsburgh, PA 15219-4785.

7. Polyethylene reference bottles, 30-mL narrow mouth to fit in a gamma well detector.

SPECIAL REAGENTS

1. Strontium carrier, 20 mg Sr mL⁻¹ - dissolve 48.4 g Sr(NO₃)₂ in 1 L of 1:99 HNO₃.
2. Yttrium carrier, 10 mg Y mL⁻¹ - dissolve 12.7 g of highest purity Y₂O₃ in a minimal amount of HNO₃; use heat if necessary. Filter, if necessary, and add water to make 1 L of solution. See the APPENDIX for the yttrium carrier counting check.
3. Iron carrier, 5 mg Fe mL⁻¹ - dissolve 5 g Fe wire in 1:1 HCl and dilute to 1 L with 1:99 HCl, or dissolve 34.7 g Fe(NO₃)₃·9H₂O in 1 L of 1:99 HNO₃.
4. Barium carrier, 10 mg Ba mL⁻¹ - dissolve 9.5 g Ba(NO₃)₂ in water and dilute to 0.5 L.
5. Barium buffer solution - 500 mL 6M acetic acid (glacial HOAC) plus 1 L of 6M NH₄OAc plus 0.5 L Ba carrier (10 mg mL⁻¹).
6. Calcium carrier, 200 mg Ca mL⁻¹ - dissolve 500 g calcium carbonate (CaCO₃) in a minimum of HCl and dilute to 1 L with water.
7. ⁸⁵Sr tracer, about 7x10⁵ Bq L⁻¹, in a well counter, this tracer should provide about 150 counts sec⁻¹ mL⁻¹.
8. Sodium carbonate solution, 1M - dissolve 106 g Na₂CO₃ in H₂O and dilute to 1L.
9. Sodium carbonate solution, 2M - dissolve 212 g Na₂CO₃ in H₂O and dilute to 1L.
10. Sodium chromate solution, 0.3M - dissolve 50 g Na₂CrO₄ in H₂O and dilute to 1L.
11. 50% sodium hydroxide solution - slowly dissolve 500 g NaOH in 500 mL of H₂O in a plastic liter bottle immersed in a beaker of ice water.

SAMPLE PREPARATION

A. Water

1. Transfer an aliquot of sample water to an appropriate sized beaker (use deionized water for the blank).
2. Add 1 mL (20 mg) strontium carrier to the blank and the sample.
3. Add exactly 1.00 mL of ^{85}Sr tracer to three 30-mL plastic bottles, the blank and the sample.
4. Fill the plastic bottles with equal volumes of 1M HCl. Set bottles aside. They will serve as references when determining the strontium yield.
5. Evaporate the samples to dryness. Add 10-mL volumes of concentrated nitric acid to the dried residue, and evaporate repeatedly to remove any trace of HCl due to the reagents added.
6. Dissolve the final residue in 8M HNO_3 . If the sample is not in a 400-mL beaker, quantitatively transfer the sample with water to a 400-mL beaker containing a Teflon-coated magnetic stirring bar. Dilute the sample to 200 mL with additional water.
7. Place the beaker on a magnetic stirrer/hot plate and stir. Adjust the pH to 5-6 with 50% NaOH. While continuing to stir, add 15 mL of 2M Na_2CO_3 . Heat the sample to just below boiling and stir for 30 min.
8. Remove the sample from the hot plate and allow the precipitate to settle overnight.
9. Place a small glass fiber filter backed with a Whatman No. 42 filter paper of the same size into a Büchner funnel. Mount the funnel on a 500 mL filter flask.
10. Filter the sample by vacuum through the funnel. Wash the carbonates retained on the filter with 1M Na_2CO_3 solution. Discard the filtrate.

11. Release the vacuum and transfer the funnel to a clean filter flask. Apply the vacuum. Dissolve the carbonates on the filter with hot 8M HNO_3 . Wash the filter with water.
12. Transfer the filtrate to a 400 mL beaker, rinsing with 8M HNO_3 . Evaporate the solution to dryness.
13. Proceed to **Determination, Fuming HNO_3 Separation**

B. Air Filters

1. Place the air filter in a 400-mL beaker (use a dry beaker for the blank).
2. Add exactly 1.00 mL of ^{85}Sr to three 30-mL plastic reference bottles, the blank and the sample.
3. Fill the plastic bottles with equal volumes of 1M HCl . Set bottles aside. (The same three reference bottles may be used for water and air filters if the analyses are done simultaneously.)
4. Add 20 mg (1 mL) strontium carrier to the blank and the sample.
5. Add 150 mL HNO_3 and 50 mL HCl . Reflux on a hot plate until clear and colorless. Evaporate to a volume of ~ 100 mL.
6. Add 100 mL of deionized water. Cool the sample to room temperature. Filter by gravity through a Whatman No. 42 filter. Wash the filter with 8M HNO_3 .
7. Evaporate the filtrate to dryness. Add 20 mL volumes of concentrated nitric acid to the dried residue, and evaporate repeatedly to remove HCl . Continue with Step 6, Section A, **Water**.

C. Soil (NaOH-HCl method) - see Note 1

1. Weigh out enough soil to generate an activity at least 10 times background (ideally 100 times) into an appropriate sized beaker containing a Teflon-coated magnetic stirring bar (see chart below). Add water to about a quarter of the beaker's volume and add 5-10 mL (100-200 mg) strontium carrier solution. Place the beaker on a magnetic stirrer.
2. To each of three 30-mL plastic reference bottles and to the sample add 1.00 mL of ^{85}Sr tracer solution. Fill the reference bottles to the same level with 1M HCl.
3. Stir the sample. While continuing to stir, add a sufficient amount of 50% NaOH to make the solution 1N NaOH. (see chart below)
4. Cover with a watch glass and stir for 10 min. Reflux overnight on a warm hot plate.
5. Remove the beaker from the hot plate and allow to cool. While stirring, cautiously add HCl, 1 mL at a time until the reaction slows, to make the solution 6M acidic (see chart below). If analyzing highly calcareous soils, an additional quantity of HCl should be added to replace the acid required to decompose the carbonates. If necessary, add a few drops of n-octyl alcohol to reduce foaming.

Activity (Bq kg ⁻¹)	Sample size (g)	Beaker size (mL)	Water (mL)	Carrier (mL)	50% NaOH (mL)	HCl (mL)
~500	5-10	250	70	5	4	90
~100	15-20	400	100	5	6	130
~50	30-40	800	200	5	11	260
~10	100	1000	250	5	14	320

6. Digest the sample overnight on a warm hot plate. Remove the beaker from the hot plate and cool.

7. Filter the sample under vacuum using a Whatman No. 42 filter paper backed by a glass fiber filter. Wash with approximately 100 mL hot 6M HCl, followed by 60 mL hot H₂O.
8. Turn off the vacuum. Return the soil residue and the filter paper to the original beaker.
9. Quantitatively transfer the filtrate and washes to an appropriate sized beaker, rinsing with water, and place on a warm hot plate to reduce the volume.
10. Remove the filtrate from the hot plate. Add 20-50 mL of HNO₃. Cover with a watch glass and place back on the hot plate. Turn the heat up to high. Continue adding HNO₃ until the conversion is complete, as indicated by the absence of brown fumes after the addition of HNO₃.
11. Add water to about a quarter of the beaker's volume to the beaker containing the filter paper and soil residue. Repeat Steps 3-7.
12. Transfer the second filtrate to the beaker containing the original filtrate. Convert to HNO₃ as in Step 10.
13. Reduce the volume of the combined filtrates to ~50 mL or until salting out begins to occur. Add ~100 mL (or twice the volume) of water, stir and cool to room temperature. If cloudy, filter under vacuum through two glass fiber filters, washing with hot 1-2M HNO₃. Discard the filters.
14. Quantitatively transfer the filtrate to a large (800-1500 mL) beaker containing a magnetic stirring bar, rinsing with water. Place the beaker on a magnetic stirrer/hot plate and stir while warming the solution.
15. Add approximately 5 g of H₂C₂O₄ (oxalic acid) L⁻¹ and continue to stir until the salt completely dissolves.
16. While stirring, adjust the pH to 5.5-6.0 with NH₄OH. If the mixture turns brown due to the presence of FeO(OH), add just enough H₂C₂O₄ to bring back the green color and readjust the pH. Repeat this process, using decreasing quantities of H₂C₂O₄, until

the last pH adjustment does not result in the brown color. (**Note:** At this point, there should be enough $\text{H}_2\text{C}_2\text{O}_4$ to precipitate the insoluble white oxalates and to complex the Fe^{+3} ion, but not enough to cause crystallization of the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ upon cooling.) Finish by adding several grams of oxalic acid as excess and adjust the pH again. Stir for 30 min on a warm hot plate.

17. Turn off the stirrer, remove the beaker from the hot plate, and allow the precipitate to settle overnight.
18. Add 5 mL of Ca carrier solution (1g Ca), stir the supernatant very gently and allow the fresh precipitate to settle for 15-20 min.
19. Filter the sample by gravity through a large Whatman No. 42 filter paper. Wash the beaker with H_2O , adding the washes to the funnel. Wash the precipitate with water until the filtrate is colorless.
20. Transfer the filter paper and precipitate to a 600-mL beaker. Add 100 mL of HNO_3 . Cover with a watch glass and wet ash the oxalates until clear and colorless or oxidation seems complete, adding more HNO_3 as necessary.
21. Add an equal volume of water and stir on a magnetic stirrer. If cloudy, filter through two glass fiber filters washing with 8M HNO_3 , followed by water. Evaporate to dryness.
22. Proceed to **Determination, Fuming HNO_3 Separations.**

Note: This method was developed at the U.S. Department of Agriculture Soil Survey Laboratory, Soil Conservation Service, Beltsville, MD. Comparative soil analyses at EML showed that the ^{85}Sr tracer could be completely equilibrated with ^{90}Sr present in the soils when consecutively treated with NaOH and HCl. The NaOH-HCl method yielded results equal to those obtained with the complete dissolution method.

D. Vegetation (dry ashing).

1. Weigh an aliquot of up to 10 g of vegetation into a tared 250-mL porcelain crucible.
(**Note:** After ashing, several aliquots can be combined to provide the desired sample

size.) Place each crucible in a muffle furnace with the crucible cover slightly ajar. Increase the temperature of the furnace at a rate of $0.80^{\circ}\text{C min}^{-1}$ to 250°C . Maintain this temperature for 30 minutes. Increase the temperature at a rate of $10^{\circ}\text{C min}^{-1}$ to 600°C . Maintain this temperature for 960 min to completely ash the sample. Cool the crucible and weigh it to determine the percent ash. Ash content for replicate crucibles should vary by not more than 4%.

2. Transfer the ashed vegetation to a beaker using 8M HNO_3 to dissolve the ash and rinse the crucible. Add 1 mL of Sr carrier (20 mg).
3. Add 1.00 mL of ^{85}Sr tracer to the blank, the sample and each of three 30-mL plastic reference bottles. Fill the bottles to the same level with 1M HCl .
4. Cover with a watch glass and reflux on a hot plate until there is no evidence of remaining organic matter, adding HNO_3 or H_2O_2 as necessary.
5. Evaporate to near dryness. Add 50 mL of 8M HNO_3 . Filter by gravity through a Whatman No. 42 filter paper into a beaker, washing with 8M HNO_3 . Continue with Step 6 below.

E. Vegetation (wet ashing).

1. Weigh an aliquot of vegetation into an appropriate sized beaker. (For 100-300 g, use a 3000-mL beaker.) Add 1 mL of Sr carrier (20 mg).
2. Add 1.00 mL of ^{85}Sr tracer to the blank, the sample and each of three 30-mL plastic reference bottles. Fill the bottles to the same level with 1M HCl .
3. Slowly add 500 mL of 8M HNO_3 . Control the foaming, if necessary, by adding a few drops of n-octyl alcohol. Cover with a watch glass and place on a low temperature hot plate overnight to maintain a slow reaction, stirring as necessary to break up the foam. Gradually increase the temperature of the hot plate, adding HNO_3 and continuing to reflux until the reaction is complete, as indicated by the absence of brown nitrogen oxide gas.

4. Remove from the hot plate. Slowly add enough HCl to equal one third the volume of HNO_3 still in the beaker. Allow the mixture to react at room temperature for 15 min, then cover with a watch glass and heat on a low temperature hot plate overnight with occasional stirring.
5. Remove the sample from the hot plate and add an equal volume of water. Allow the sample to cool to room temperature. Filter by gravity through a large Whatman No. 42 filter paper into a beaker. Wash with 8M HNO_3 .
6. Evaporate the filtrate to dryness. Dissolve the residue in a minimum of 8M HNO_3 . Quantitatively transfer the solution to a 400-mL beaker containing a Teflon-coated magnetic stirring bar, rinsing with H_2O . Dilute the solution to 200 mL with additional H_2O .
7. Place the beaker on a magnetic stirrer/hot plate and stir. Adjust the pH to 5-6 with 50% NaOH. While continuing to stir, add 15 mL of 2M Na_2CO_3 . Heat the sample to just below boiling and stir for 30 min.
8. Remove the sample from the hot plate and allow the precipitate to settle overnight.
9. Place a small glass fiber filter backed by a Whatman No. 42 filter paper of the same size into a Büchner funnel. Mount the funnel on a 500 mL filter flask.
10. Filter the sample by vacuum through the funnel. Wash the carbonates retained on the filter with 1M Na_2CO_3 solution. Discard the filtrate.
11. Release the vacuum and transfer the funnel to a clean filter flask. Apply the vacuum. Dissolve the carbonates on the filter with hot 8M HNO_3 . Wash the filter with water.
12. Transfer the filtrate to a 400 mL beaker, rinsing with 8M HNO_3 . Evaporate to dryness.
13. Proceed to **Determination, Fuming HNO_3 Separations.**

DETERMINATION

A. Fuming HNO_3 separations.

1. Dissolve the residual salt in H_2O and some fuming HNO_3 , while stirring on a magnetic stirrer. When dissolved, add additional fuming HNO_3 to precipitate $\text{Sr}(\text{NO}_3)_2$. The first two separations require concentrations of $> 75\%$ HNO_3 , subsequent separations require less HNO_3 (see chart below). Water and air filters usually require two separations. Large quantities of soils with a high Ca content may require up to five or more fuming HNO_3 separations.

Separation	Water (mL)	Fuming HNO_3 (mL)	% HNO_3	final volume (mL)
1st	40	25 + 195	80.1	260
2nd	60	25 + 195	76.0	280
3rd	40	25 + 115	75.4	180
4th	30	105	75.4	135
5th	23	77	74.9	100

2. Place a dry (very important to prevent sample loss) 5.5-cm glass fiber filter (for smaller volumes a 4.25-cm filter) in a dry Büchner funnel and mount the funnel in a 1-L filter flask.
3. Suction filter the sample into the flask. Turn off the vacuum. Transfer the funnel to a Fisher filtrator, placing an appropriate sized beaker underneath (for the last filtration, use a 40-mL heavy-wall conical centrifuge tube (C-tube)). Apply a vacuum while dissolving the precipitate on the filter with water into the beaker. Use additional water to complete the transfer of any residue in the original beaker to the funnel and subsequently into the beaker or C-tube. Proceed with Step 4 or 5.
4. Evaporate the sample solution to dryness if another fuming HNO_3 separation is desired, and repeat Steps 1 to 3 using smaller volumes as indicated in the chart.

5. If the sample solution is now in a C-tube, place the tube in a hot water bath and adjust the volume to ~20 mL. Proceed with **First Milking**.

B. First milking.

1. Add 1 mL of iron carrier solution to the separated strontium fraction in the centrifuge tube. Stir the solution and place the tube in a 90°C water bath to warm.
2. While stirring, adjust the pH of the sample to 8 with NH_4OH . Remove the stirring rod, rinsing with H_2O . Remove the centrifuge tube from the water bath and cool to room temperature in a cold water bath.
3. Centrifuge the sample at 2000 rpm for 5 min. Decant the supernate into a second 40-mL centrifuge tube. Reserve the supernate for Step 6 and note the hour and date of this initial OH^- precipitation as **first milk separation time**.
4. Dissolve the precipitate in the first centrifuge tube in a few drops of HCl and dilute to 10 mL with H_2O . Stir the solution and warm the tube in the hot water bath.
5. While stirring, adjust the pH of the sample to 8 with NH_4OH . Remove the stirring rod, rinsing with H_2O . Remove the centrifuge tube from the water bath and cool to room temperature in a cold water bath.
6. Centrifuge the sample at 2000 rpm for 5 min. Decant and combine the supernate with the supernate reserved from Step 3. Evaporate to reduce the volume to 20 mL. Discard the precipitate.
7. While stirring, add 4 mL of barium buffer solution to the sample. If necessary, adjust the pH of the sample to 5.5 with either 6M HCl or NH_4OH (see **Note 1**).
8. Return the centrifuge tube to the hot water bath. While stirring vigorously, add 1 mL of 0.3M Na_2CrO_4 dropwise to the sample (see **Note 2**). Allow the sample to digest in the hot water bath for 10 min or longer to allow a good precipitate to form.
9. Remove the stirring rod, rinsing with H_2O . Remove the sample tube from the hot water bath and cool in a cold water bath.

10. Centrifuge the tube at 2000 rpm for 5 min. Decant the supernate into a 30-mL polyethylene bottle. Discard the precipitate.
11. Add 10-15 drops of HCl and exactly 1.00 mL of yttrium carrier solution to the sample in the polyethylene bottle and enough water to bring the volume of the solution to the same level as in the reference bottles.
12. Proceed to **Strontium-85 yield determination**.

Notes:

1. The pH of the solution is critical at this point. Complete precipitation of BaCrO_4 will not occur in a more acidic solution and strontium will partially precipitate in more basic solutions.
2. If large quantities of barium are present in the sample, only a partial precipitation of the Ba as BaCrO_4 may occur. The sample is centrifuged and the supernate decanted into another 40-mL centrifuge tube. The precipitation is completed by the dropwise addition of 0.3M Na_2CrO_4 to the supernate and the analysis is continued with Step 10.

C. Strontium-85 yield measurement.

1. Measure the activity of the three reference aliquots, the blank and the sample with a NaI(Tl) crystal gamma detector, collecting at least 10^4 counts.
2. After subtracting the background counts, calculate the ^{85}Sr yield of the sample by dividing the sample counts by the average of the three reference counts.
3. Store the sample for 2 weeks to allow ^{90}Y to reach secular equilibrium with ^{90}Sr (see **Note**).

Note: The **first milk separation time** noted in Step 3, **First milking**, is the start of the yttrium ingrowth period. In order to correct for less than complete buildup of ^{90}Y , a correction factor is included in the calculations.

D. Second milking.

1. Quantitatively transfer the sample from the polyethylene bottle to a 40-mL, heavy-walled, conical centrifuge tube with a minimum of H_2O . Stir the solution and place the tube in a 90°C water bath to warm.
2. While stirring, adjust the pH of the sample to 8 with NH_4OH . Add six drops of H_2O_2 and heat for 1 h. Remove and rinse the stirring rod. Remove the centrifuge tube from the water bath and cool to room temperature in a cold water bath.
3. Centrifuge the sample for 5 min at 2000 rpm. Decant the supernate into another 40-mL centrifuge tube. Record the hour and date of the precipitation as **second milk separation time**.
4. Dissolve the precipitate in the centrifuge tube with a few drops of HCl and stir. Dilute the sample to 15 mL with H_2O . Stir the solution and warm the tube in the hot water bath.
5. While stirring, adjust the pH of the sample to 8 with NH_4OH . Remove and rinse the stirring rod. Remove the centrifuge tube from the water bath and cool to room temperature in a cold water bath.
6. Centrifuge the sample for 5 min. Decant and combine the supernate with the supernate reserved from Step 3. Return the combined supernates to the hot water bath and reduce the volume to 20 mL. Transfer to a 30-mL polyethylene bottle and set aside for possible future milking.
7. Add four drops of HCl to the precipitate and stir until it dissolves. Add 25 mL of H_2O , stir and heat in the hot water bath.
8. Add 1 mL of strontium carrier (20 mg Sr) to serve as a holdback carrier. While stirring, adjust the pH to 8 with NH_4OH .
9. Remove and rinse the stirring rod. Remove the sample tube from the hot water bath and cool in a cold water bath.

10. Centrifuge the tube at 2000 rpm for 5 min. Decant and discard the supernate.
11. Add three drops of HCl to dissolve the precipitate, and 25 mL of H₂O.
12. Stir the sample and place the tube in a hot water bath. Add 1 mL of saturated H₂C₂O₄ (oxalic acid) solution.
13. Adjust the pH to 2-3 by the dropwise addition of NH₄OH with vigorous stirring. Digest the sample in the hot water bath for 1 h.
14. Rinse and remove the stirring rod from the tube, and cool it to room temperature in cold water.
15. Centrifuge the tube at 2000 rpm for 10 min. Decant and discard most of the supernate.
16. Dry a 2.8-cm Whatman No. 42 filter paper on a 110°C hot plate or in an 110°C oven, cool and weigh to the nearest 0.1 mg.
17. Using a Teflon filter funnel assembly, filter the precipitate by suction through the weighed 2.8-cm Whatman No. 42 filter paper, backed by a 2.8-cm glass fiber filter, completing the transfer with a minimum amount of water. Wash the precipitate with 95% ethanol.
18. With the suction on, remove the filter funnel. Carefully separate the Whatman filter with the precipitate from the glass fiber filter backing. Place the filter paper with the precipitate on a 110°C hot plate. Turn off the vacuum and discard the glass fiber filter. Discard the filtrate.
19. Dry the filter with precipitate to a constant weight to determine the gravimetric yield.
20. Carefully mount the filtered precipitate on a nylon disc, cover with Mylar, and fasten the assembly with a nylon ring.
21. Measure the sample in a low-level gas flow proportional counter, recording the hour and date of the beginning of the measurement period.

22. Collect at least 10,000 counts, disregarding the first 200 min (2 cycles) of counting to eliminate possible interference from any ^{222}Rn progeny present due to the filtration process. Proceed to calculations.

E. Gravimetric yttrium yield measurement.

1. Standardize triplicate 10-mL aliquots of the original yttrium carrier solution each time a fresh batch is made by precipitating the oxalate as described above and filtering through a fine (grade F), tared, sintered, glass filter crucible that has been dried to a constant weight.
2. Determine the weight of the yttrium oxalate precipitated from the sample as described in Steps 15-19 of **Second Milking**. The yttrium yield is the ratio of the weight of the sample oxalate to the standardized weight of the oxalate precipitated from the carrier solution.

CALCULATIONS

The β counting data obtained from the ^{90}Y precipitate must be corrected to give the activity of the ^{90}Sr in the sample. The corrections include those for ingrowth of ^{90}Y , counter background, ^{90}Y efficiency, strontium yield, yttrium yield, and ^{90}Y decay. ^{90}Y beta emissions are very energetic and are always counted with approximately the same mass of precipitate, so no correction for self-absorption is necessary.

The strontium yield is ordinarily determined by measuring the recovery of ^{85}Sr tracer added to the sample. Since the ratio of sample counts to counts from an aliquot of the original ^{85}Sr tracer solution is used to determine yield, there is no need to know the radioactivity rate of the tracer or to apply decay corrections for ^{85}Sr .

The activity of a sample of ^{90}Sr over a time interval, t , is

$$\int_0^t A dt' = \int_0^t A_0 e^{-\lambda t'} dt'$$

where A_0 is the initial activity of the sample. Integrating and rearranging to solve for A_0 yields:

$$A_0 = \left(\int_0^t A dt' \right) \cdot \frac{\lambda}{1 - e^{-\lambda t}}$$

The half-life of ^{90}Sr is quite large (29 y), so A_0 is essentially constant throughout the period of chemical separation and analysis. After 2 weeks, a sample of ^{90}Sr will be in secular equilibrium with its daughter, ^{90}Y , and the activities of the two nuclides will be equal. The quantity under the integral sign in the last equation above is the (corrected) measured activity of the separated ^{90}Y over the time period from separation to end of counting:

$$\int_0^t A dt' = \frac{N_y - B \cdot dt_c}{R_y \cdot R_{Sr} \cdot I_y \cdot D_y \cdot E_c}$$

To obtain A_0 , this quantity is multiplied by the factor

$$\frac{\lambda_Y}{1 - e^{-\lambda_Y \cdot dt_c}}$$

where:

λ_Y = decay constant of ^{90}Y (0.0108 h^{-1})

dt_c = total count time minus two 100-minute cycles (see **Note**)

N_y = total counts from all cycles except the first two (see **Note**)

B = counter background for the matrix used (^{90}Y -oxalate)

R_y = yttrium yield fraction

R_{sr} = strontium yield fraction

I_y = ^{90}Y ingrowth fraction = $1 - e^{-0.0108 \cdot dt1 \rightarrow 2}$ = fraction of ^{90}Y produced during the time from extraction of ^{90}Sr ("1st milk") to separation of ^{90}Y from ^{90}Sr ("2nd milk").

D_y = ^{90}Y decay fraction = $e^{-0.0108 \cdot dt2 \rightarrow c_0}$

E_c = counter efficiency for ^{90}Y -oxalate (counts min^{-1} dpm^{-1})

$dt1 \rightarrow 2$ = 1st milk to 2nd milk time

$dt2 \rightarrow c_0$ = 2nd milk time to start of counting plus two 100-min cycles (see **Note**)

Note: The first two cycles are ignored to allow for the decay of short-lived beta-emitting daughters from any radon-222 that may have attached to the Y-oxalate mount during preparation.

The calculated activity of the blank is subtracted from the calculated activity of the sample. The result is converted to appropriate units and divided by the sample size to obtain the activity concentration of the sample.

To check the radiochemical purity of the ^{90}Y -oxalate precipitate, a weighted linear regression analysis is done on the counting data, with $\text{Ln}(\text{counts} - \text{background counts})$ plotted against time. The weighting factor is the variance of the dependent variable:

$$\text{Weighting factor} = \text{Var}(\ln(c - c_{bkg})) = \frac{c + (\sigma_{c_{bkg}})^2}{(c - c_{bkg})^2}$$

where:

- C = sample counts
 C_{bkg} = background counts
 σ_{Cbkg} = standard deviation of background counts

The slope of the weighted regression line is equal to λ_Y , the decay constant of ^{90}Y . The value for λ_Y obtained from the regression analysis is compared to the known value of 0.0108 h^{-1} .

All calculations are done by computer.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	40
Counter Background	(cps)	0.005
Yield (Sr)	(%)	80
Yield (Y)	(%)	95
Blank	(cps)	
LLD (400 min)	(Bq)	0.007
LLD (1000 min)	(Bq)	0.004

APPENDIX

YTTRIUM CARRIER COUNTING CHECK

To verify that the carrier solution contains only stable yttrium, complete the following procedure:

1. Pipette 1 mL of yttrium carrier into each of three 40-mL centrifuge tubes. Dilute to 20 mL with H₂O.
2. Heat in a water bath to about 90°C. While stirring, adjust the pH to 8 with NH₄OH. Digest for 10 min and cool in a cold water bath.
3. Centrifuge for 5 min. Decant and discard the supernate. Proceed with Steps 11-22 of **Second Milking**.

Sr-04-RC

STRONTIUM-90 IN WATER CONTAINING OTHER RADIOISOTOPES BY Cerenkov COUNTING

Contact Person(s) : Salvatore C. Scarpitta

APPLICATION

The following procedure is used in the EML Quality Assessment Program (QAP; Sanderson and Greenlaw, 1996) for water or gross alpha/beta samples containing ^{90}Sr . This procedure was developed by Jimmy Chang, Institute of Nuclear Energy Research, Taiwan, and was tested at EML using NIST $^{90}\text{Sr}/\text{Y}$ reference materials and ^{90}Sr contained in QAP water samples. It allows for the rapid determination of ^{90}Sr ($\beta_{\text{max}} = 0.546 \text{ MeV}$) via its progeny, ^{90}Y ($\beta_{\text{max}} = 2.27 \text{ MeV}$) in aqueous solutions by Cerenkov counting (see Procedure Ba-01-R; Scarpitta and Fisenne, 1996).

Cerenkov counting is applicable for β particles with maximum energies $> 0.263 \text{ MeV}$. Alpha and gamma emitting nuclides are not detected. Immediately following separation of ^{90}Y from ^{90}Sr , a baseline count rate, C_b , is obtained to quantify any Cerenkov contribution by other nuclides that may be present in the sample.

Yield recovery is determined by adding 30 mg of Sr^{+2} carrier to the sample or by gamma counting the added ^{85}Sr tracer. The sample is Cerenkov counted at any two time intervals, t_1 and t_2 , to measure the ingrowth of ^{90}Y above C_b . Strontium-90 is calculated from the ingrowth of ^{90}Y . The Cerenkov counting efficiency for ^{90}Y in water is about 65-70%, whereas that of ^{90}Sr is $< 0.3\%$ for a 0-15 keV Cerenkov counting window. For a 20-min count time, the detection limit is about 6 mBq mL^{-1} (0.16 pCi mL^{-1}) or 0.35 dpm mL^{-1} with a relative standard deviation $< 3\%$.

SPECIAL APPARATUS

Packard Tri-Carb 2250-CA liquid scintillation spectrometer

SPECIAL REAGENTS

1. NIST traceable $^{90}\text{Sr}/\text{Y}$ reference standard of known activity (about 1000 dpm g^{-1}) to determine the ^{90}Y Cerenkov counting efficiency.
2. TRU Resin - Eichrom Industries, 8205 Cass Ave., Suite 107, Darien, IL 606651.

DETERMINATION

1. Dispense about 8-16 Bq of ^{90}Sr gravimetrically into either a 20 mL low ^{40}K borosilicate glass or plastic scintillation vial (see **Note 1**).
2. Add 10 mL of deionized water.
3. Prepare a blank using 10 mL of water.
4. Count both samples three times for 10-min each using the net average count rate to determine the ^{90}Y counting efficiency, $E^{90}\text{Y}$ (counts min^{-1} dpm $^{-1}$).
5. Preset the Packard Tri-Carb to Protocol 4 for Cerenkov determinations (Scarpitta and Fisenne, 1996). (**Note:** The Cerenkov counting window is typically 0-15 keV, although the full window, 0-2000 keV, may be used with a 50% increase in background.)
6. Obtain a sample containing an unknown amount of ^{90}Sr .
7. Add 30 mg of Sr^{++} carrier (as nitrate) to the sample for yield recovery.
8. Prepare an identical vial containing water as a Sr^{++} reference standard.

9. Reduce a premeasured amount, M_g (g), of sample to be tested to 10 mL to improve counting statistics.

Note :

1. A wavelength shifter, ANSA (7-Amino 1,3 Naphthalene di-Sulfonic Acid) can be used to enhance the Cerenkov counting efficiency but is not recommended if strontium yield recovery is to be determined gravimetrically. Nuclides that produce a Cerenkov signal in 25 mM ANSA are shown in Figure 1 (see Scarpitta and Fisenne, 1996).

SEPARATION

1. Separate the ^{90}Y from the ^{90}Sr by either oxalate precipitation (see Procedure Sr-03-RC) or EiChrom's TRU Spec extraction chromatographic resin. Record the separation date and time, t_0 .
2. Obtain a net baseline count rate for C_b immediately following ^{90}Y separation, using Protocol No. 4 on the Packard Tri-Carb 2250 CA counter and the Cerenkov counting window (0-15 keV).

CALCULATIONS

1. Recount the ^{90}Sr fraction three times a day over a 2-day period using the count rates (counts min^{-1}) CT_1 , CT_2 and CT_3 to calculate the ^{90}Sr activity in Step 2. The times t_1 , t_2 and t_3 are the number of hours after ^{90}Y separation in Step 1 of **Separation**.
2. Use the ^{90}Sr calculation as follows when ^{89}Sr is not present in the sample. (**Note:** A Basic computer program is provided in the Appendix to perform the ^{90}Sr calculations.)

$$A_1^{90}\text{Sr} (Bq\text{ kg}^{-1}) = \frac{(CT_2 - CT_1) - C_b}{60 \times M_S \times E^{90}\text{Y} \times [\exp\{-\lambda(t_1 - t_0)\} - \exp\{-\lambda(t_2 - t_0)\}]} \quad (1)$$

$$A_2 \text{ } ^{90}\text{Sr} \text{ (Bq kg}^{-1}\text{)} = \frac{(CT_3 - CT_1) - C_b}{60 \times M_s \times E \text{ } ^{90}\text{Y} \times [\exp\{-\lambda(t_1 - t_0)\} - \exp\{-\lambda(t_3 - t_0)\}]} \quad (2)$$

where

λ = ^{90}Y decay constant - 0.01083 h⁻¹

$E \text{ } ^{90}\text{Y}$ = ^{90}Y Cerenkov counting efficiency (counts min⁻¹ dpm⁻¹)

M_s = mass of sample (kg)

3. Obtain the average of the two ^{90}Sr activity concentrations, A_1 and A_2 from Step 2.
(**Note:** A third count could be obtained with Equation 2 if modified accordingly.)
4. Using the sample vial and the Sr^{+2} reference standard, precipitate the strontium as the carbonate, filter, dry and weigh each to obtain the yield recovery. Correct the value obtained in Step 3, dividing by the yield recovery factor. (**Note:** Gamma emitting ^{85}Sr can be added to the sample in Step 7 of **Determination** instead of Sr^{+2} .)

REFERENCES

Sanderson, C. G. and P. Greenlaw

“Semi-Annual Report of the Department of Energy, Office of Environmental Management, Quality Assessment Program”

USDOE Report EML-581, July (1996)

Scarpitta, S. C. and I. M. Fisenne

“Cerenkov Counting as a Complement to Liquid Scintillation Counting”

Appl. Radiat. Isot., 47, 795-800 (1996)

Scarpitta, S. C. and I. M. Fisenne

“Calibration of a Liquid Scintillation Counter for Alpha, Beta and Cerenkov Counting”

USDOE Report EML-583, July (1996)

Cerenkov Efficiency in 10 ml of 25 mM ANSA (Plastic Vials)

% Efficiency (0-50 keV)

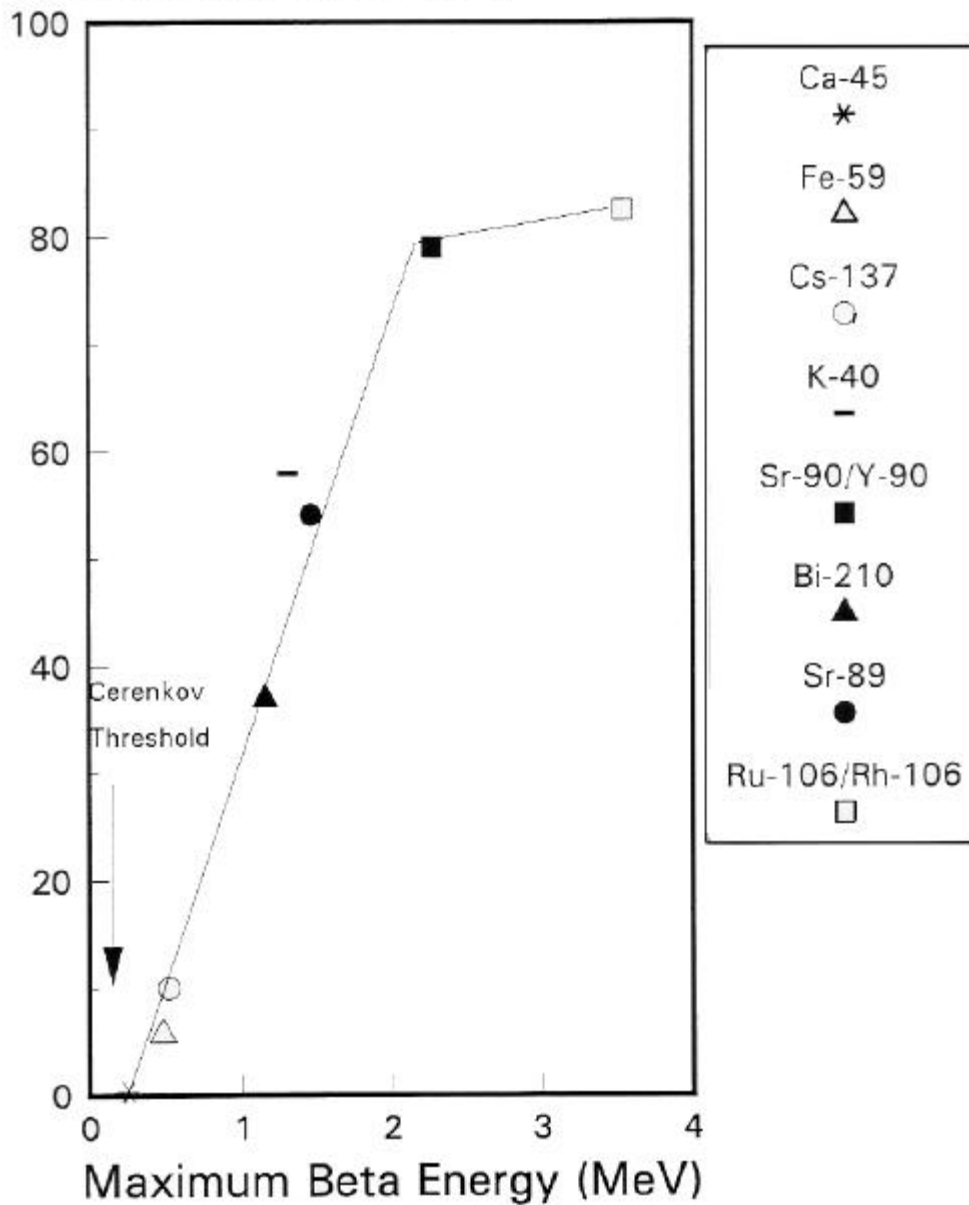


Figure 1. Cerenkov efficiency in 10 mL of 25 mM ANSA (plastic vials).

APPENDIX

Basic Computer Program

```

10  REM "SR90CER.BAS" BY J.CHANG METHOD
20  REM CALCULATE 90SR ACTIVITY(DPM) FOR A SAMPLE USING CERENKOV COUNTING
50  TITLES--"Test of Cerenkov Method Using 895 dpm of NIST 90-Sr Standard"
60  COUNTIMES="10 min"
100 REM ENTER TIME DATA HERE
120 DELT1=.75 ' HRS
122 DELT2=19.22
124 DELT3=111.6
130 REM ENTER COUNT RATES HERE
132 CT1=36.5
134 CT2=159.1
136 CT3=514.4001
150 LAMBD2=.01083 ' HR-1
160 EFFY90=.82 ' CPM/DPM
200 REM CALCULATE SR90 ACTIVITY(DPM) HERE
205 DF1=EXP((-LAMBD2*DELT1))-EXP((-LAMBD2*DELT2))
210 A1SR90=(CT2-CT1)/(DF1*EFFY90)
255 DF2=EXP((-LAMBD2*DELT1))-EXP((-LAMBD2*DELT3))
260 A2SR90=(CT3-CT1)/(DF2*EFFY90)
500 REM PRINT RESULTS
510 CLS:SCREEN 2:KEY OFF
520 PRINT DATES;" ";
525 PRINT "STRONTIUM-90 RESULTS BY Sr-SPEC and CERENKOV COUNTING":PRINT
530 PRINT TAB(10);TITLES:PRINT
535 PRINT TAB(15);"Count Time = ";COUNTIMES;TAB(40);"Y-90 Efficiency = ";EFFY90:
    PRINT:PRINT
540 PRINT "Data":PRINT
550 PRINT TAB(1);"Del T1";TAB(10);"Cnt T1";TAB(30);"Del T2";TAB(40);"Cnt T2";TAB(60);"Del T3";TAB(70);"Cnt T3"
555 PRINT TAB(1);" (hr) ";TAB(10);" (cpm) ";TAB(30);" (hr) ";TAB(40);" (cpm) ";TAB(60);" (hr) ";TAB(70);" (cpm)":PRINT
557 PRINT TAB(1);DELT1;TAB(10);CT1;TAB(30);DELT2;TAB(40);CT2;TAB(60);DELT3;TAB(70);CT3
560 PRINT:PRINT:PRINT:PRINT "Sr-90 Results";
570 PRINT TAB(30);A1SR90;" dpm";TAB(60);A2SR90;" dpm"
575 PRINT TAB(1);"Obs/Exp";TAB(30);A1SR90/895;" ";TAB(60);A2SR90/895;
580 PRINT:PRINT:PRINT

```

02-21-1995 STRONTIUM-90 RESULTS BY Sr-SPEC and CERENKOV COUNTING

Test of. Cerenkov Method Using 895 dpm of NIST 90-Sr Standard

Count Time -- 10 min Y-90 Efficiency -- .82

Data

Del T1 (hr)	Cnt T1 (cpm)	Del T2 (hr)	Cnt T2 (cpm)	Del T3 (hr)	Cnt T3 (cpm)
.75	36.5	19.22	159.1	111.6	514.4001
Sr-90 Results		831.421 dpm		840.6198 dpm	
Obs/Exp		.928962		.9392401	

Ok

Technetium

Tc-01-RC

TECHNETIUM-99 IN WATER AND VEGETATION
(see Volume II)

Thorium

Th-01-RC

THORIUM IN URINE
(see Volume II)

Uranium

U-01-RC

ENRICHED URANIUM IN URINE
(see Volume II)

U-02-RC

**ISOTOPIC URANIUM IN BIOLOGICAL
AND ENVIRONMENTAL MATERIALS**

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure has been used to analyze soft tissue, vegetation, water, and air filter samples (Hindman, 1983; Sill and Williams, 1981; Welford et al., 1960).

Uranium from acid leached, dry-ashed and wet-ashed materials is equilibrated with ^{232}U tracer, and is isolated by anion exchange chromatography. The separated U isotopes are microprecipitated for α spectrometry.

SPECIAL APPARATUS

1. Ion exchange columns (see Specification 7.5).
2. Polyethylene dispensing bottles (see Specification 7.11).
3. Special apparatus for the microprecipitation of U are listed under the generic procedure, G-03.

SPECIAL REAGENTS

1. Uranium-232 tracer solution - about 0.3 Bq g^{-1} of solution in a dispensing bottle.
2. Bio Rad AG 1-X4 (100-200 mesh), anion exchange resin (see Specification 7.4).

SAMPLE PREPARATION

A. Vegetation and soft tissue.

1. Dry ash the sample according to the method described in Procedure Sr-02-RC (see **Note 1**).
2. Weigh out 10 g of ash and transfer to a 400-mL beaker.
3. Add a weighed amount of ^{232}U tracer solution (~ 0.03 Bq) from the dispensing bottle (see **Note 2**).
4. Add 200 mL of HNO_3 to the beaker and evaporate slowly to dryness.
5. Add 25 mL of HNO_3 to the beaker. Repeat the acid addition and evaporation until a white residue is obtained. (**Note:** If silicious material is present, transfer the sample to a 100 mL platinum dish or a 100 mL Teflon beaker with HNO_3 . Add 10 mL of HF to the vessel and evaporate to dryness. Repeat additions of 25 mL HNO_3 - 10 mL HF as necessary to volatilize the silica. Remove the HF by adding three successive 10-mL volumes of HNO_3 to the vessel and evaporate to dryness.)
6. Add 25 mL of HCl and evaporate to dryness. Repeat the acid addition and evaporation twice more.
7. Heat to dissolve the residue in 50-100 mL of 7N HCl.
8. Continue with **Determination**.

B. Water.

1. Evaporate the H_2O sample to a small volume.
2. Add a weighed amount of ^{232}U tracer solution (~ 0.017 Bq) from a dispensing bottle and evaporate slowly to dryness (see **Note 2**).

3. Add 50 mL of HNO_3 and evaporate to dryness. Add 25 mL of HNO_3 and evaporate twice more.
4. Dissolve the residue in 25 mL of HCl and evaporate to dryness. Repeat the HCl addition and evaporation.
5. Heat to dissolve the residue in ≤ 50 mL of 7N HCl .
6. Continue with **Determination**.

C. Air filters.

Cellulose filters:

1. Add a weighed amount of ^{232}U tracer solution (~ 0.017 Bq) from a dispensing bottle to the filter in a platinum dish and dry ash in an electric muffle at 550°C (see **Note 2**).
2. Dissolve the residue in HNO_3 and transfer to a 250-mL beaker.
3. Add 25 mL of HNO_3 and evaporate to dryness. Repeat the acid addition and evaporation twice more.
4. Dissolve the residue in 25 mL of HCl and evaporate to dryness. Repeat the HCl addition and evaporation twice more.
5. Heat and dissolve the residue in ≤ 50 mL of 7N HCl .
6. Continue with **Determination**.

Glass fiber filters:

1. Place the filter and a magnetic stirring bar in a 400-mL Teflon beaker. Add a weighed amount of ^{232}U tracer solution (~ 0.033 Bq) from a dispensing bottle.
2. Add 100 mL of HNO_3 , mechanically stir while heating for 1 h. Reduce the solution volume to ~ 25 mL. Remove the stirring bar and rinse with H_2O .

3. Add 10 mL of HF and evaporate to dryness.
4. Repeat the 25 mL HNO₃ - 10 mL HF additions and evaporations as necessary to volatilize the silica.
5. Add 25 mL of HNO₃ to the beaker and evaporate to dryness. Repeat twice more.
6. Heat and dissolve the residue in 25 mL of HCl and evaporate to dryness. Repeat the HCl addition and evaporation twice more.
7. Dissolve the residue in ≤ 50 mL of 7N HCl.
8. Continue with **Determination**.

DETERMINATION

1. Pass the 7N HCl sample solution obtained during sample preparation through a prepared anion exchange column (see **Note 3**). Discard the column effluent.
2. Wash the column with 400 mL of 7N HCl. Discard the washings.
3. Elute the uranium with 200 mL of 1N HCl, collecting the eluate in a 250-mL beaker. Discard the resin.
4. Evaporate the eluate to near dryness.
5. Destroy any residual organic material with dropwise additions of HNO₃.
6. Evaporate the solution to dryness. Dissolve the residue in a few drops of HCl.
7. Convert the solution to the chloride with three 5-mL additions of HCl.
8. Add 1-2 mL of 1N HCl, prepared with filtered water (see Procedure G-03, Microprecipitation Source Preparation for Alpha Spectrometry). Cool to room temperature.

9. Continue the analysis under Procedure G-03, Microprecipitation Source Preparation for Alpha Spectrometry.

Notes:

1. Freeze-dried or wet tissue may be wet ashed directly in HNO₃. Proceed with Step 3 of **Vegetation and Soft Tissue**.
2. It is necessary to analyze reagent blanks with each batch of samples to correct the U results.
3. 20 mL of Bio-Rad AG1-X4, prepared according to Specification 7.4 are conditioned with 500 mL of 7N HCl.

LOWER LIMIT OF DETECTION (LLD)

Uranium Isotopes

Counter Efficiency	(%)	40
Counter Background	(cps)	3.33x10 ⁻⁶ for ²³⁸ U 3.33x10 ⁻⁶ for ²³⁴ U
Yield	(%)	85
Blank	(cps)	3.33x10 ⁻⁶ for ²³⁸ U 3.33x10 ⁻⁵ for ²³⁴ U
LLD (400 min)	(mBq)	0.0002 for ²³⁸ U 0.0005 for ²³⁴ U
LLD (1000 min)	(mBq)	0.0001 for ²³⁸ U 0.0003 for ²³⁴ U
LLD (5000 min)	(mBq)	0.0005 for ²³⁸ U 0.0001 for ²³⁴ U

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U-03-RC

ISOTOPIC URANIUM IN BONE ASH

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure has been used to analyze 50 g human bone ash samples (Fisenne et al., 1980; Hindman, 1983; Sill and Williams, 1981).

Bone ash is dissolved in acid, and the U is equilibrated with ^{232}U tracer and isolated by solvent extraction. The purified U isotopes are microprecipitated for α spectrometry.

SPECIAL APPARATUS

1. Mechanical shaker.
2. Polyethylene dispensing bottle - see Specification 7.10.
3. Special apparatus for the microprecipitation of U are listed under the generic procedure, G-03.

SPECIAL REAGENTS

1. Uranium-232 tracer solution - about 0.1 Bq g^{-1} of solution in a dispensing bottle.
2. Alamine-336, tertiary tricapyryl amine (Henkel Corporation, 2430 N. Huachuca Dr., Tucson, AZ 85745-1273) 3:7 in toluene. Wash twice with an equal volume of 1:1 HCl. Prepare 100 mL of acid-washed 3:7 Alamine-336 for each sample.

3. Standardized sodium hydroxide 0.1N - dissolve 4 g of NaOH in H₂O and dilute to 1 L. Standardize the solution against potassium acid phthalate.
4. Phenolphthalein indicator - dissolve 0.5 g of reagent in 100 mL of 95% ethanol.

SAMPLE PREPARATION

1. Weigh 50 g of ground, dry-ashed bone and transfer to a 400-mL beaker.
2. Add a weighed amount of ²³²U tracer (~ 0.01 Bq per sample) from the dispensing bottle. (**Note:** It is necessary to analyze reagent blanks with each batch of samples to correct the U results.)
3. Add 100 mL of HCl and heat gently on a hot plate for 10 min with occasional stirring.
4. Add 70 mL of H₂O and stir to obtain a clear solution. If insoluble material is present, filter the sample through a glass fiber filter. Wash the filter with 1:1 HCl and discard the residue.
5. Cool the solution. Transfer a 100-μL aliquot of the sample into a 150-mL beaker containing 25 mL of H₂O. Add two to three drops of 0.5% phenolphthalein indicator. Stir and titrate the solution with 0.1N NaOH to the pink endpoint. Calculate the normality of the sample solution.
6. If the normality is >5.8N in HCl, proceed directly to the extraction. If the normality is <5.8N, transfer the sample to a 250-mL graduated cylinder and record the volume. Return the sample to the beaker and add an appropriate volume of HCl to the cylinder to increase the sample acid concentration to 6N. Transfer the acid to the sample beaker and proceed with the extraction.

DETERMINATION

1. Transfer 50 mL of acid-washed Alamine-336 into each of two 500-mL separatory funnels.
2. Transfer the sample to the first separatory funnel. Wash the beaker with 1:1 HCl and add the washings to the funnel.
3. Shake the separatory funnel for 5 min. Allow the phases to separate and draw off the aqueous (lower) phase into the second separatory funnel. Retain the organic phase in the first funnel.
4. Shake the second separatory funnel for 5 min. Allow the phases to separate, draw off, and then discard the aqueous (lower) phase.
5. Combine the two organic phases in one of the separatory funnels.
6. Wash the organic phase four times for 5 min with equal volumes of 1:1 HCl. Discard the washings.
7. Strip the U from the organic phase by shaking twice for 5 min with 100-mL portions of 0.1N HCl. Combine the strip solutions in a 400-mL beaker.
8. Evaporate the solution to near dryness.
9. Destroy any residual organic material with dropwise additions of HNO₃.
10. Evaporate the solution to dryness. Dissolve the residue in a few drops of HCl.
11. Convert the solution to the chloride with three 5-mL additions of HCl.
12. Add 1-2 mL of 1N HCl, prepared with filtered water (see Procedure G-03, Microprecipitation Source Preparation for Alpha Spectrometry). Cool to room temperature.
13. Continue the analysis under Procedure G-03, Microprecipitation Source Preparation for Alpha Spectrometry.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	40
Counter Background	(cps)	3.33×10^{-6} for ^{238}U 6.67×10^{-6} for ^{234}U
Yield	(%)	90
Blank	(cps)	3.33×10^{-6} for ^{238}U 3.30×10^{-5} for ^{234}U
LLD (400 min)	(mBq)	0.2 for ^{238}U 0.5 for ^{234}U
LLD (1000 min)	(mBq)	0.1 for ^{238}U for ^{234}U
LLD (5000 min)	(mBq)	0.05 for ^{238}U 0.1 for ^{234}U

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U-04-RC

URANIUM IN BIOLOGICAL AND ENVIRONMENTAL MATERIALS
(see Volume II)
